WADC TECHNICAL REPORT 54-13
PART II
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INVESTIGATION OF THE EFFECT OF RAW MATERIAL PRODUCTION VARIABLES ON THE PHYSICAL AND CHEMICAL PROPERTIES OF CARBIDES, NITRIDES AND BORIDES

H. BLUMENTHAL

AMERICAN ELECTRO METAL CORPORATION

JUNE 1955

WRIGHT AIR DEVELOPMENT CENTER

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AMERICAN ELECTRO METAL CORPORATION

JUNE 1955

MATERIALS LABORATORY
CONTRACT No. AF 33(616)-89
PROJECT No. 7350

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Carpenter Litho & Prtg. Co., Springfield, O.
700 - 11 January 1956

FOREWORD

This report was prepared by the American Electro Metal Corporation under USAF Contract No. AF 33(616)-89. The contract was initiated under Project No. 7350, "Ceramics and Cermet Materials", Task No. 73500, "Ceramic and Cermet Materials Development", formerly RDO No. 615-17, "Ceramic Materials", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt Normand Hyman acting as project engineer.

This report is the second part of WADC Technical Report 54-13. The first part of this report, dated June, 1954, was published under the basic report number only; it should be considered as Part I although it was not so marked.

This report covers work conducted from September 1953 to September 1954.

ABSTRACT

Section I. Study of Titanium Carbide Powders

The chemical analyses of pure grade commercial titanium carbides were very similar as far as the main constituents were concerned. The differences were only in the oxygen, free carbon and impurity content.

Particle size reduction by ball milling was found to be independent of the ball milling medium and a function only of ball milling time, size and kind of the ball mill, and ball-to-load ratio.

Procedures were worked out for the determination of particle size distribution of a fine powder and for a flotation of such a material, which removed free carbon.

Section II. Properties of Unbonded Titanium Carbide Bars

Titanium carbide powders without binder addition were hot pressed to high densities and tested for electrical resistivity and corrosion resistance.

It was found that a decrease in particle size, addition of up to 1% of free carbon, and acid leaching influenced densification beneficially.

Leaching of a ball milled powder before hot pressing or higher densities of the hot pressed bars decreased electrical resistivity.

The only corrosion product found by chemical analysis when TiC or 90/10 TiC/WC bars were exposed to air at 1000°C was TiO_2. There was probably a formation of WO_3 which partly volatilized.

Section III. Infiltration of TiC Skeletons

Pieces of low densities were infiltrated with liquid cobalt and nickel and the factors governing infiltrability were studied. It was found that an oxide film surrounding the individual carbide particles was beneficial for good infiltration.

Section IV. Investigation of Bonded Titanium Carbide Bars

Dense nickel bonded titanium carbide bars were produced by hot or cold pressing of ball milled powders followed by vacuum sintering. Various factors determining densification and transverse rupture strength, such as the presence of oxygen, free carbon, iron and other carbides as well as ball milling, pressing and sintering procedures were investigated. It was found that the relationship of these factors to the physical properties of final

bars changed considerably with the origin of the titanium carbide used as starting material.

Section V. The Microstructure of Titanium Carbide

A metallographic study was carried out in order to link physical properties to microstructure. It could be shown that microstructure, grain shape and grain growth were functions of three interrelated factors: production procedure of the titanium carbide, surface conditioning of the particles and impurities in the powder. An explanation of the "coring effect", long observed in cemented carbides, was given, based on the assumption of an oxide film surrounding the individual particles.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M.R. Whitmore
Technical Director
Materials Laboratory
Directorate of Research

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INTRODUCTION

The aim of this project was to investigate the effect of raw material production variables on the physical and chemical properties of carbides, nitrides and borides. These materials are of interest because of their good mechanical properties at elevated temperatures. As the number of variables to be studied was very large, it was agreed to restrict this investigation to one material only. The material selected was titanium carbide.

Titanium carbide is readily available in various purities and grades, depending upon production procedures and raw materials. It was believed that duplicating commercial production procedures in the laboratory would not result in materials identical with those actually produced commercially. Various titanium carbides, produced commercially by as many different procedures as possible, were, therefore, purchased and used for this investigation.

The main impurities of all titanium carbides studied are free carbon, oxygen and nitrogen. It appears that no one has succeeded, so far, in making completely pure titanium carbide even in test tube quantities. While such material would be highly interesting from a theoretical point of view, the inability to produce it commercially would exclude it from this investigation. Other impurities found in commercial materials are due to the starting materials used. Production procedure and comminution treatment also contribute impurities.

This report is divided into five sections. The first section is devoted to a study of the as-received titanium carbide materials. Studies of chemical composition, the effect of ball milling and the purification of fine powders by leaching and flotation were made.

The second section deals with hot pressing of unbonded titanium carbide bars. Measurements of their electrical resistivity and corrosion resistance were obtained.

The third section deals with infiltration of titanium carbide skeletons.

The fourth section is mainly an investigation of the effect of various impurities as follows:

Impurities were added to as received materials in various quantities and their influences on the physical properties of dense nickel-bonded compacts, produced by powder metallurgy techniques, were investigated. By this "addition technique" the influences of free carbon, iron, TiO and various carbides were studied.

Another way to study the influence of impurities was to reduce them gradually or eliminate them entirely. This was done with free carbon, which was reduced by a flotation procedure, and with iron and TiO_2, both of which could be removed to a certain degree by leaching with acids.

This section also contains investigations on the effects of ball milling and pressing procedures and the influence of various ball milling media.

In Section V, microstructures of titanium carbide bars produced in different ways are given and an attempt is made to evaluate structures in the light of physical performance of the respective bars.

SECTION I

STUDY OF TITANIUM CARBIDE POWDERS

A. Materials Used in this Investigation

All commercial processes of titanium carbide production at the present time utilize the chemical reaction of titanium dioxide and carbon to form as nearly as possible stoichiometric TiC according to the equation

$$TiO_2 + 3\ C = TiC + 2\ CO.$$

This reaction is carried out in practice in three ways:

1. In a menstruum of molten metal[1)]
2. In the solid state, either under the cover of a protective atmosphere[2)] or in vacuum[3)], or
3. In an arc melting operation[4,5)]

For experimental purposes titanium carbide has been produced by reacting titanium metal or titanium hydride with carbon, by fused salt electrolysis and by a few other methods. According to its formula, TiC, titanium carbide has the stoichiometric composition of 79.97% Ti and 20.03% C. The actual amount of carbon combined with titanium in the commercial products, however, is between 17% and 19.5% and there is always a certain amount of free carbon present ranging from 0.1% to 3%, which even with repeated heating at high temperature does not combine with titanium. Since, at least, some oxygen and nitrogen, which are not removable by chemical means, are also present, it can be safely assumed that commercial titanium carbide is a solid solution of TiC, TiO and TiN. Production variables, such as starting materials, heating time and cycle, temperature, production procedure, etc., vary the amount of combined carbon, oxygen and nitrogen in titanium carbide.

Five different titanium carbides, representing the above production processes, were used in this investigation. They are identified in Table 1 and their chemical and spectrographic analyses are given in Table 2.

TABLE 1

INVESTIGATED MATERIALS

Code	Supplier	Production Procedure
K	Kennametal, Inc. Latrobe, Pa.	Menstruum process
R	Metallwerk Plansee Reutte, Austria	Solid state reaction under protective atmosphere
MC	Metro-Cutanit London, England	Solid state reaction in vacuum
T	Titanium Alloy Mfg. Co. Niagara Falls, N. Y.	Arc melting, pure product
N	Norton Company Worcester, Mass.	Arc melting, technical product

All chemical analyses were done in our own laboratories, using standard procedures. Oxygen determinations were made by vacuum fusion (see Fig. 1). Spectroscopic analyses were carried out by Lucius Pitkin, a New York commercial laboratory, and X-ray diffraction analyses by Dr. B. Post, Polytechnic Institute of Brooklyn.

Several shipments were received from some of the suppliers. Their chemical analyses varied slightly especially as far as impurities were concerned. The analyses given in Table 2 are for those lots which were used for most of the experiments.

The first four materials were used in the as-received condition. Material N-3, received in lumps, was crushed to -100 mesh and carried through a flotation procedure in order to bring its free carbon content in line with the other products.

The nickel powder used as binder and infiltrant was carbonyl nickel of 9 to 14 microns particle size and a purity of 99.5%, supplied by A. D. Mackay, Inc., New York.

The cobalt used as infiltrant was electrolytic powder of -200 mesh, supplied by African Metals Corp., New York.

Titanium monoxide was produced by reacting TiO_2 with TiH_2. Some was supplied by Lt. Winter of WADC.

Titanium nitride was supplied by Metal Hydrides, Inc., Beverly, Mass.

TABLE 2

CHEMICAL COMPOSITION OF COMMERCIAL TITANIUM CARBIDES

Supplier Code	Kennametal K-2	Metallwerk R-2	Metro-Cutanit MC-1	Titanium Alloy T-3	Norton Co. N-3[1]
Ti	79.7	79.0	79.0	79.1	78.0
C comb	19.4	19.0	19.0	19.1	16.8
C free	0.21	0.73	0.54	0.20	0.45
O_2	0.10	0.09	0.16	0.57	1.93
N_2	0.15	0.97	0.67	0.45	0.86
Fe	0.06	0.13	0.11	0.22	1.54
Mo	—	0.19[2]	—	—	—
W	—	0.12[2]	—	—	—
Zr	x 0.1[2]	0.05[2]	—	—	—
Cu	x 0.01[2]	—	x 0.01[2]	x 0.01[2]	x 0.001[2]
Al	x 0.01[2]	—	—	—	0.1[2]
Mn	x 0.01[2]	—	—	x 0.01[2]	—
Si	x 0.01[2]	x 0.01[2]	—	x 0.1[2]	0.1[2]
Mg	—	0.01[2]	—	x 0.01[2]	x 0.03[2]
Total	99.76	100.30	99.49	99.77	99.81
$\frac{C\ comb}{Ti + C\ comb}$	19.6	19.4	19.4	19.5	17.7

x Less than
1) Flotation purified
2) Spectrographic analysis

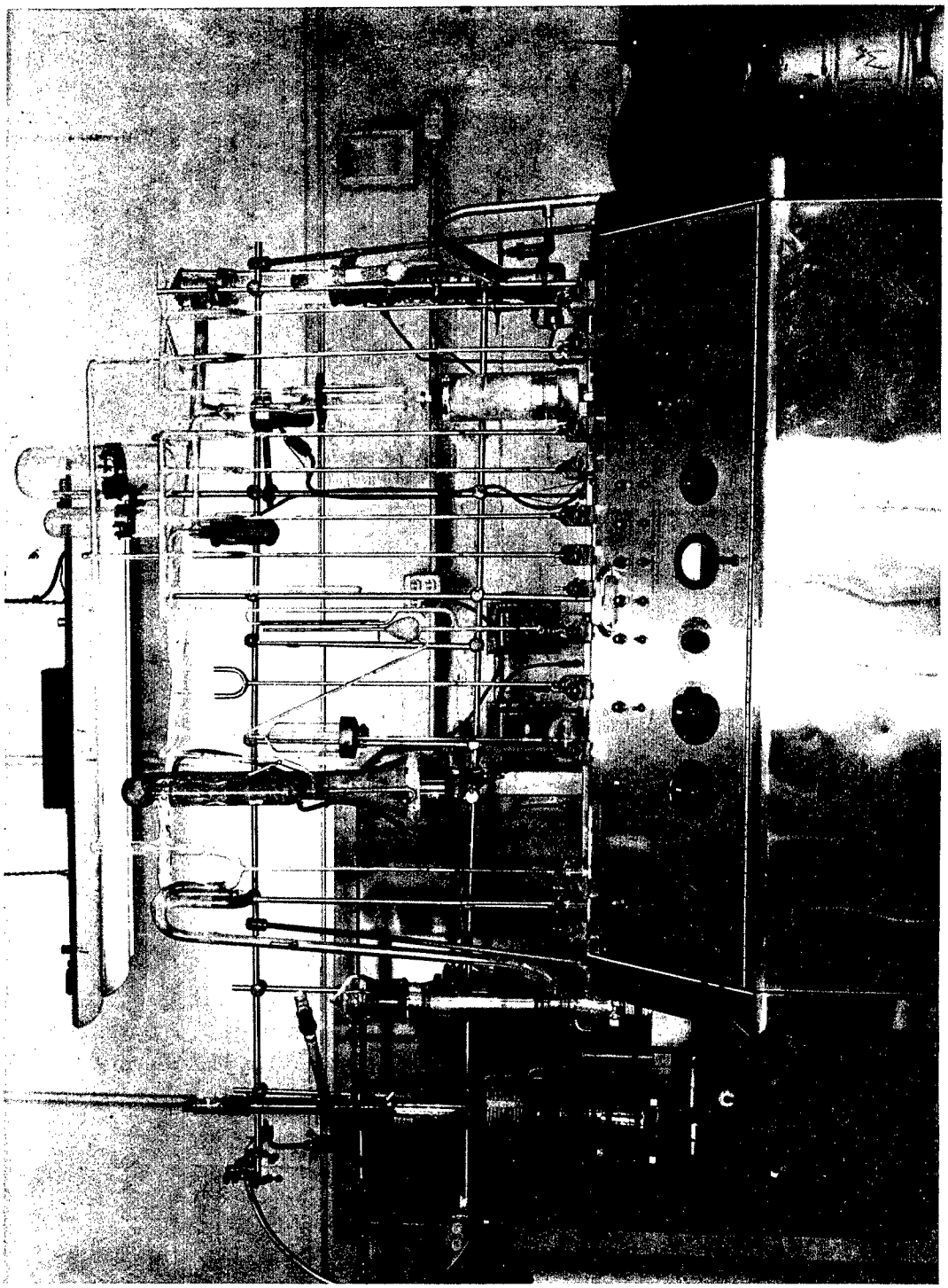


Fig. 1 Vacuum Fusion Apparatus

B. Effect of Ball Milling Medium on Particle Size Reduction and Chemical Composition

Introduction

The aim of this study was threefold, namely, to investigate

1. whether the particle size reduction during ball milling was influenced by the ball milling medium,
2. to what extent the ball milling medium affected the pickup of impurities,
3. whether an acid leach of the product ball milled in a steel mill would restore the original analysis

Experiments

Ball milling was done in air, argon, water, ethyl alcohol, acetone, xylene, carbon tetrachloride, and trichloroethylene. A steel ball mill of one liter capacity was used, the load was 250 grams of powder and 1500 grams of steel balls of various sizes. Ball milling was stopped after a certain time and samples for particle size determination and chemical analysis were taken out. The ball mill was then closed again and milling continued up to 64 hours. The ball mill was opened in this way thirteen times during the run of each experiment.

To compare the effects of this interrupted ball milling procedure with the results of continuous ball milling, uninterrupted ball milling was done for 16 hours in air, water and acetone.

Ball milling was done in a tungsten carbide mill (with tungsten carbide balls) in air, water, and acetone for 16 and 72 hours.

The powders ball milled in liquid media were filtered and vacuum dried. All powders were chemically analyzed for iron or tungsten and some for oxygen. The powders ball milled in the steel mill were leached twice with hot 1-3 hydrochloric acid, washed with hot water, vacuum dried and analyzed.

The amounts of liquids used in all experiments were just enough to cover balls and powder completely. A Fisher Sub-Sieve Sizer was used for average particle size determinations.

Results

1. Particle size reduction was essentially a function of time and independent of the ball milling medium (Table 3). Only during the first five hours particle sizes jumped somewhat irregularly, from there on reduction was fairly regular and almost identical for all investigated media.

2. Iron pickup was affected to a great extent by the ball milling medium (Table 4). The pickup was less in argon than in air and considerably less in dry ball milling than in wet ball milling. The kind of liquid used also influenced the pickup.

3. Table 5 and Fig. 2 show the oxygen pickup during ball milling in air, argon and acetone. As expected, oxygen pickup was considerably

TABLE 3

REDUCTION OF PARTICLE SIZE DURING BALL MILLING IN DIFFERENT MEDIA

(Kennametal TiC in Steel Mill, Average Particle Size in Microns)

Time (Hrs)	Air	Argon	Water	Ethyl Alcohol	Acetone	Xylene	Carbon Tetra-chloride	Trichloro-ethylene
0	32	32	32	32	32	32	32	32
1	22	22	21.5	18.6	27.8	19.6	24	25.4
2	14.3	16	15.0	11.6	11.3	12.9	18	18.7
3	11.0	11.6	11.7	10.3	10.5	11.4	12.8	13.8
4	9.0	9.0	8.8	7.9	6.4	8.5	11.2	9.9
5	6.8	7.6	8.0	7.3	6.1	8.3	--	8.1
6	5.7	6.5	6.8	7.0	5.8	7.4	8.3	8.0
7	4.9	6.0	6.2	6.7	5.2	6.9	7.8	7.7
8	4.2	5.1	5.1	--	4.4	6.2	6.8	7.5
10	3.7	4.3	4.4	6.0	4.3	4.7	6.2	5.1
13	2.9	3.4	3.5	4.9	4.2	4.4	5.2	3.9
16	2.6	2.9	3.1	--	4.0	4.1	3.6	3.6
32	1.7	2.1	2.5	2.2	2.4	2.6	3.1	2.5
64	1.4	1.4	2.1	1.6	1.5	1.8	1.8	1.7

TABLE 4

IRON PICKUP DURING BALL MILLING IN DIFFERENT MEDIA

(Kennametal TiC, % Fe after Ball Milling for Various Lengths of Time)

Time (Hrs)	Air	Argon	Water	Ethyl Alcohol	Acetone	Xylene	Carbon Tetra-chloride	Trichloro-ethylene
0	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
1	0.28	0.25	0.47	0.40	0.32	0.38	0.28	0.32
2	0.41	0.31	0.89	1.27	0.86	0.80	0.63	0.51
5	0.70	0.62	2.06	2.51	2.21	1.52	1.36	2.40
8	1.07	0.83	3.88	4.03	2.54	2.81	3.73	3.42
16	1.42	1.20	7.87	9.81	5.69	5.56	7.40	8.75
32	1.62	1.52	11.0	12.5	11.0	10.5	10.4	11.5
64	1.78	1.80	13.6	19.2	18.25	19.7	22.0	18.15

TABLE 5

OXYGEN PICKUP DURING BALL MILLING IN DIFFERENT MEDIA

(Kennametal TiC, % Oxygen after Ball Milling for Various Lengths of Time)

Time (Hrs)	Air	Argon	Acetone
0	0.10	0.10	0.17
8	0.26	—	—
16	0.40	0.18	0.50
32	0.63	—	—
64	0.85	—	—
72	—	0.32	1.16

TABLE 6

IRON PICKUP AND PARTICLE SIZE IN INTERRUPTED AND CONTINUOUS BALL MILLING FOR 16 HOURS

(Kennametal TiC)

	Iron Pickup (%)		Particle Size (Microns)	
	Interrupted	Continuous	Interrupted	Continuous
Air	1.42	0.92	2.6	4.6
Water	7.87	3.55	3.1	4.4
Acetone	5.69	3.32	4.0	4.9

TABLE 7

% WC PICKED UP DURING BALL MILLING IN TUNGSTEN CARBIDE MILL

(Kennametal TiC)

Time (Hrs)	Air	Water	Acetone
16	—	6.56	6.44
72	2.71	9.37	10.03

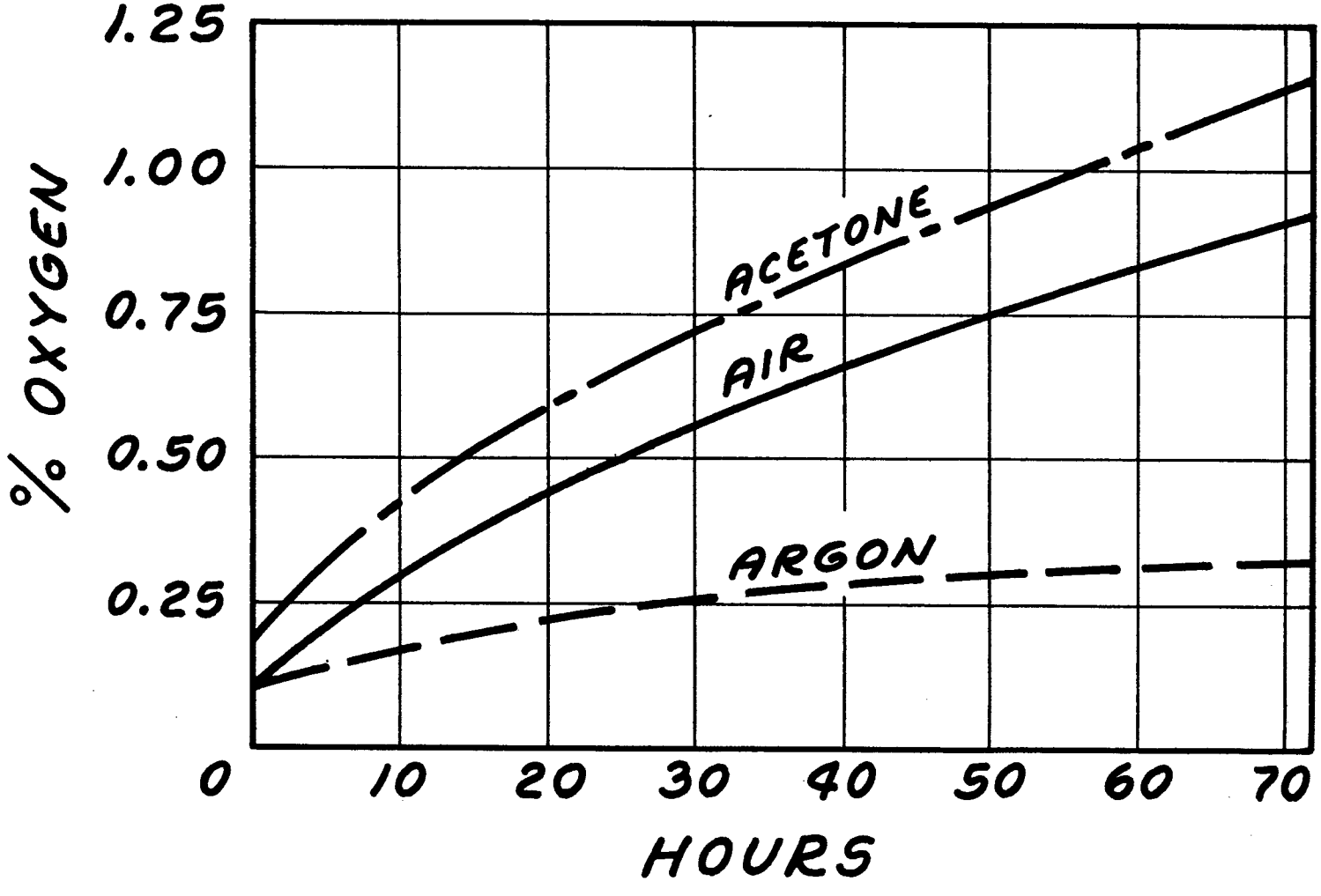


FIG. 2 OXYGEN PICKUP DURING BALL MILLING IN DIFFERENT MEDIA

higher in air than in argon. In wet ball milling the oxygen pickup was much higher than in dry ball milling.

Pickup was greatly enhanced by interrupting the ball milling and opening of the ball mill, as Table 6 shows. Particle size reduction was greater when ball milling was interrupted, especially when ball milling was done in air.

The amount of tungsten carbide picked up during ball milling in a tungsten carbide mill also varied considerably with time and ball milling medium, as Table 7 shows. Here, too, the pickup in the liquid media was much higher than in dry ball milling.

4. The analyses of the powders ball milled in the steel mill and leached with hydrochloric acid are compared with the analysis of the original material in Table 8. The only notable differences were a somewhat increased free carbon content and a higher oxygen content, especially for the powder ball milled for 238 hours in air.

TABLE 8

ANALYSES AFTER BALL MILLING IN DIFFERENT MEDIA AND LEACHING WITH HYDROCHLORIC ACID COMPARED WITH ORIGINAL ANALYSIS

(Kennametal TiC in Steel Mill)

Medium	Air[1]	H_2O[2]	CCl_4[2]	C_2HCl_3[2]	C_2H_5OH[2]	As Rec'd
Ti	79.6	79.3	79.6	79.0	79.2	79.7
C_{comb}	19.3	19.3	19.8	19.4	19.3	19.4
C_{free}	0.40	0.39	0.37	0.42	0.04	0.21
Fe	0.12	0.14	0.24	0.08	0.11	0.06
N_2	0.25	0.24	0.18	0.21	0.14	0.15
O_2	0.68	0.24	0.15	0.12	0.18	0.10
Total	100.35	99.61	100.34	99.33	98.97	99.53
$\frac{C_{comb}}{Ti + C_{comb}}$	19.5	19.6	19.9	19.7	19.6	19.6

1) Ball milled 238 hours
2) Ball milled 64 hours

Discussion

The reason for the greater particle size reduction experienced in interrupted ball milling was that by opening of the ball mill and removing of a sample the cake formed on top and bottom of the mill was broken up and subjected to a more severe ball milling action. Caking was especially noticeable in air. The increase of iron pickup due to the interruption was very pronounced, it amounted to about 100%. The air admitted during each

opening of the ball mill enhanced the attack on the balls and on the mill. The iron pickup was not only due to mechanical but also to chemical action. An inert atmosphere should, therefore, reduce the iron pickup. According to Table 4 this in fact happened, but only for short ball milling times. The reason for this was found in the fact that the ball mill was not completely airtight. The reason for the diminishing rate of iron pickup in dry ball milling might be that mill and balls became coated with titanium carbide powder and that this coating became denser and more protective with time. Ball milling in a liquid medium destroyed this coating and the pickup of iron increased. There was, however, also an individual influence of the various liquids on the iron pickup which was due to chemical reactions of the liquid alone or in connection with the oxygen of the air on mill and balls. The influence of air plus liquid was most obvious in ball milling in water, where the pickup rate decreased considerably when the ball mill stayed closed for 16 and 32 hours (see last two lines of Table 4).

That the ball milling medium exercised a chemical influence on the titanium carbide is obvious from Table 5 which shows an increased oxygen pickup of the powder in acetone compared with air and argon. The results for ball milling in argon made it quite certain that either the ball mill was leaking or that the air was not completely replaced by argon. It is quite probable that a small amount of air is occluded by the starting material which is not replaceable by argon.

The oxygen pickup during ball milling for 62 hours in a steel mill varied between 0.85% in air and 2.88% in carbon tetrachloride. It was almost completely removable by a leaching process and chemical analyses showed that the removed oxygen was in the form of TiO_2 (see the following chapter).

Conclusions

1. Particle size reduction is a function of time and independent of ball milling medium.

2. Oxygen, iron and WC pickup are a function of ball milling time. Organic liquids are more corrosive towards a steel mill than water. Iron and WC pickup in a gas filled ball mill is lower than in one containing liquid by a factor between 3 and 10.

3. The pickup during ball milling is due not only to mechanical but also to chemical forces as is shown by the increased contamination during interrupted ball milling compared with continuous ball milling and the differences in oxygen pickup in different media.

4. At least part of the oxygen picked up by ball milling can be removed by an acid leach. This leach also removes titanium at the same time, indicating that a chemical reaction between the oxygen of the air and TiC has taken place in the ball mill.

5. The ball milled and acid leached powders have a somewhat higher oxygen and free carbon content than the original TiC, but the amount of combined carbon has not changed.

C. Removal of Oxygen by a Hydrochloric Acid Leach

Experiments

Powders from various sources ball milled in different ball mills and different media were analyzed for their oxygen content before and after leaching with hydrochloric acid. The spent acid was analyzed for titanium.

Results

Although the amount of oxygen which the powders contained after ball milling varied between 0.4% and 2.4%, the ratio of oxygen to titanium removed by leaching was constant and corresponded to the formula TiO_2. (Stoichiometric TiO_2 has 40% O_2). Table 9 tabulates the results.

Conclusions

1. During ball milling, TiC is oxidized to a certain degree. The degree of oxidation depends upon the kind of powder and the ball milling conditions.

2. Oxidation causes the formation of TiO_2, very probably in the form of a surface film around the individual particles.

3. Not all of the oxygen picked up during ball milling is removable even with repeated leaching. It is strongly believed that the oxide fraction not removable by leaching is in solid solution with TiC.

D. Determination of Particle Size Distribution

Introduction

Particle sizes of titanium carbide powders mentioned in this report were determined with the Fisher Sub-Sieve Sizer, and it is believed that the results obtained with this apparatus are well reproducible for the same kind of powder. If, for instance, equal amounts of one particular TiC powder were ball milled under the same conditions for an equal length of time, the average particle sizes measured with the apparatus were the same. It is, therefore, easy to read from a graph the ball milling time necessary to produce a desired particle size. If, however, the same amount of TiC was mixed with 10% graphite and now ball milled under the same conditions, the average particle size measured was much lower than the actual particle size of the TiC, due to the presence of the graphite. In order to determine the true particle size of TiC in such a case, and in order to determine the particle size distribution, which might be an important factor in many investigations, the following method was used.

Method

The powder was hot pressed to a low density, keeping the temperature as low as possible in order to avoid grain growth. The piece was mounted in Bakelite and polished. It was viewed under the microscope with a filar micrometer eye piece, which made it possible to move the vertical cross

TABLE 9

REMOVAL OF TiO_2 BY HYDROCHLORIC ACID LEACH

Powder No.	Lot No.	% O_2 As Rec'd	Ball Milling Procedure	% O_2 As B'milled	Loss during Leach		
					% O_2	% Ti	$O_2/Ti+O_2$
—	K-1*	0.19	WC mill, 72 hrs, acetone	1.16	0.59	0.89	40
218	N-3	0.64	Steel mill, 32 hrs, air	2.39	0 .47	0.65	42
223	K-4	0.14	Steel mill, 48 hrs, air	0.58	0.15	0.21	42
229	R-1	0.09	Steel mill, 48 hrs, air	0.39	0.25	0.36	41

* The letters indicate the manufacturer:
K: Kennametal, Inc.
N: Norton Company
R: Metallwerk Plansee

hair over the field of vision while the horizontal cross hair was stationary. All particles which were cut by the horizontal line were counted. Their "diameter", the distance between intersection of the vertical and horizontal cross hairs when the former was moved across the particle, was measured with the aid of the filar micrometer dial. Fig. 3 illustrates this procedure.

Experiments

1. The particles of six fields of a bar pressed from Kennametal powder were counted, measured and recorded in five ranges, proceeding in geometrical progression. The "diameters" of all counted particles were added and divided by the number of particles counted, which amounted to 143.

2. The same original powder was ball milled with 10% additional graphite for the same length of time; 130 particles were counted.

Results

1. Table 10 shows the particle size distribution in each of six fields and the total particle size distribution. The average particle diameter was found to be 2.62 microns. The Fisher Sub-Sieve Sizer had shown an average particle size of 2.05 microns.

2. Table 11 shows the result of the second experiment. The particle size distribution was somewhat different probably due to the presence of the fine graphite particles and the average particle diameter was found to be 2.28 microns. The Fisher Sub-Sieve Sizer indicated in this case an average particle size of 1.55 microns.

Discussion

The results of the two experiments were in agreement with each other as far as the average particle size diameters were concerned. If the very low and the very high particle sizes were disregarded, the particle size distribution was also not too far apart considering that the amount of particles counted was very small. Comparing the results of the Fisher Sub-Sieve Sizer with those obtained in these experiments, large differences were encountered, especially in the second experiment. This is very understandable. The Fisher apparatus measures the air permeability of a slightly compacted powder which is highly influenced by the presence of graphite particles, while the micro-count disregards these particles completely.

Conclusion and Remarks

It is believed that the described procedure represents a fairly simple and fast method to determine particle size distribution of sub-sieve size powders. The number of fields and particles counted should, however, be increased for higher accuracy.

It might be more convenient and less strenuous to the operator to take pictures of the fields with a superimposed grating at high magnification instead of counting the particles under the microscope.

Due to the pressure of other work this particular investigation was not further pursued.

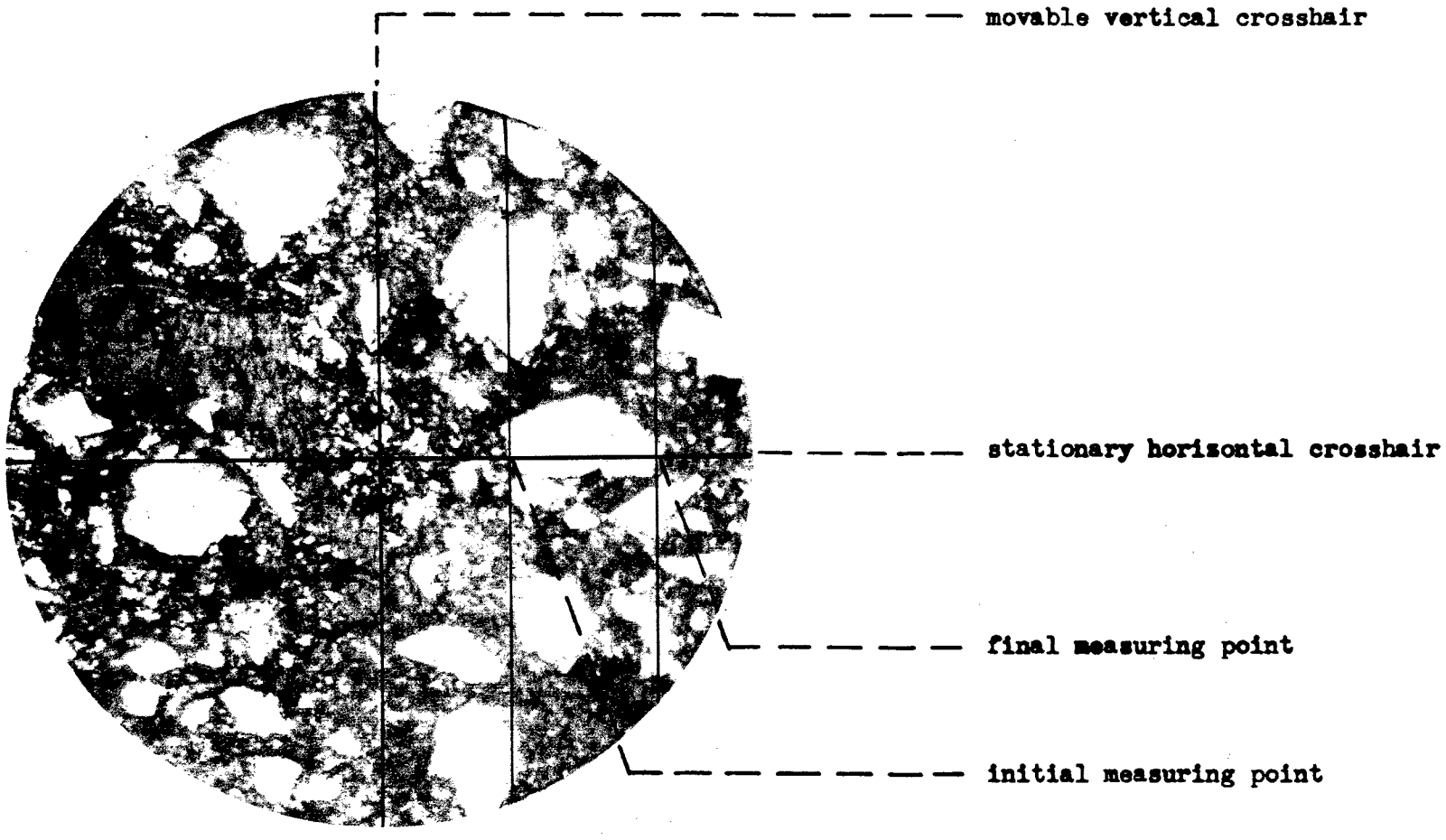


Fig. 3 Determination of Particle Size Distribution

TABLE 10. PARTICLE SIZE DISTRIBUTION OF POWDER 100C

(Hot Pressed at 1400° C to about 75% of Theoretical Density)

Particle Size Microns	Field 1 N*)	%	Field 2 N	%	Field 3 N	%	Field 4 N	%	Field 5 N	%	Field 6 N	%	Total N	%
0.2 - 0.5	0	0	2	7.1	0	0	0	0	0	0	0	0	2	1.4
0.5 - 1.25	5	22.8	8	28.6	7	38.8	10	35.7	5	19.2	10	47.6	45	31.5
1.25 - 3.15	11	50	13	46.4	9	50	10	35.7	12	46.2	5	23.7	60	41.9
3.15 - 7.80	3	13.6	1	3.6	1	5.6	7	25	9	34.6	4	19.1	25	17.5
7.80 - 19.5	3	13.6	4	14.3	1	5.6	1	3.6	0	0	2	9.6	11	7.7
Total	22		28		18		28		26		21		143	

TABLE 11 PARTICLE SIZE DISTRIBUTION OF POWDER 146

(Hot Pressed at 1700° C to about 82% of Theoretical Density)

Particle Size Microns	Field 1 N*)	%	Field 2 N	%	Field 3 N	%	Field 4 N	%	Field 5 N	%	Field 6 N	%	Total N	%
0.2 - 0.5	3	10.3	1	5.6	1	4.5	0	0	2	10	2	10.5	9	6.9
0.5 - 1.25	12	41.4	8	44.5	11	50	9	40.9	9	45	6	31.6	55	42.4
1.25 - 3.15	8	27.6	6	33.3	4	18.2	9	40.9	5	25	8	42.1	40	30.8
3.15 - 7.80	5	17.2	2	11.1	4	18.2	1	4.5	1	5	1	5.3	14	10.8
7.80 - 19.5	1	3.5	0	0	1	4.5	3	13.6	3	15	2	10.5	10	7.7
19.5 - 49	0	0	1	5.6	1	4.5	0	0	0	0	0	0	2	1.6
Total	29		18		22		22		20		19		130	

*) N = Number of Particles

E. Flotation

Introduction

All commercial titanium carbide powders contain certain amounts of uncombined carbon or graphite. It was one of the tasks of this project to investigate its influence on the physical properties of finished pieces. A flotation procedure[6] was used in order to reduce the free carbon content. This procedure consisted in mixing material of fine particle size in a flotation cell with water and a few drops of pine oil which acted as a frothing agent. The graphite was carried off in the "overflow" while the bulk of the purified carbide stayed behind in the flotation cell as "tailings".

It was found that the flotation procedure described had two shortcomings. A large amount of titanium carbide was carried over into the overflow and as a consequence, the end of the flotation could not be observed. The process had to be interrupted after an arbitrarily chosen time and the amount of tailings and overflow could not be predicted. This made the procedure non-reproducible.

Experiments

1. Norton (N-2) powder of -325 mesh was flotation purified using the above procedure
   a) by refloating the tailings of the previous flotation run
   b) by refloating tailings and overflow of the previous run.
2. Titanium Alloy (T-2) TiC received in lumps was crushed to -100 mesh and then submitted to flotation.
3. Kennametal powder of 0.14% free carbon was flotation purified in order to reduce this impurity content still further.
   a) Powder was floated in the as-received condition.
   b) As-received powder was ball milled for 42 hours to 2.5 microns and then floated.
   c) The tailings of floated as-received powder (see a) were ball milled 42 hours and refloated.
4. Experiments were undertaken to improve the flotation procedure
   a) by adding various reagents into the flotation cell
   b) by changing the load in the flotation cell.

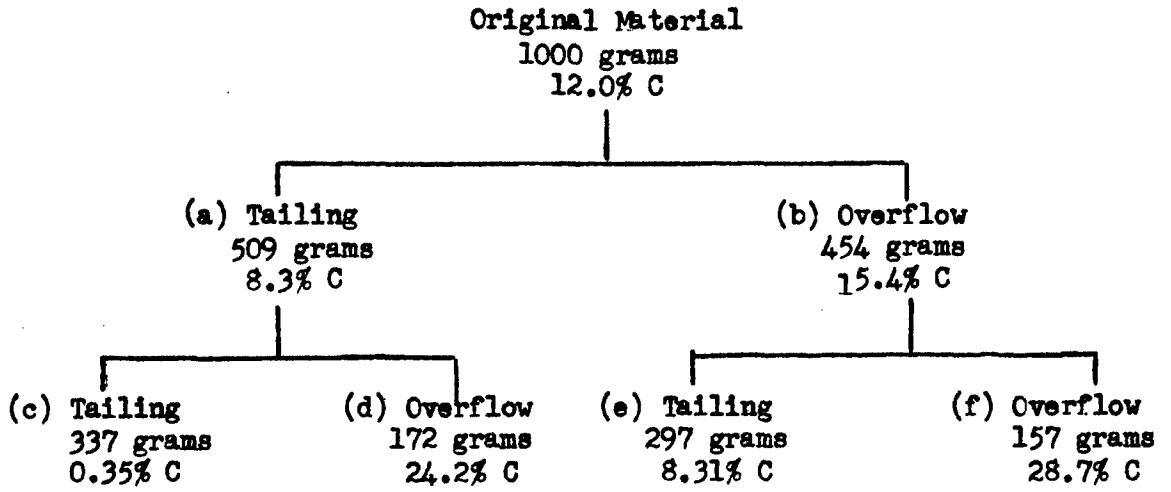
Results

1. a) By refloating the tailings of the previous run, Norton Company's titanium carbide free carbon content was reduced in three steps from 12.0% to 6.53%, 2.0% and finally 0.37%.

1. b) Results of refloating of tailings and overflow are given in Fig. 4. The figure shows that about one-third of the original material had a low free carbon analysis. By combining the tailings of the overflow flotation with those of the first flotation (a + e) and both overflows of the second flotations with each other (d + f) and continued refloating both fractions, higher yields of low graphite containing TiC could be obtained.

2. The free carbon content of Titanium Alloy's crushed TiC could be reduced in one flotation from 2.7 to 0.2%.

3. The results of the flotation of Kennametal TiC are given in



FLOTATION OF A HIGH GRAPHITE CONTAINING MATERIAL

FIG. 4

Tables 12, 13 and 14. They show:

a) A completely graphite-free TiC was not obtained even when the starting material had as low a free carbon content as 0.04%. The procedure yielded instead graphite-enriched overflows and graphite-depleted tailings.
b) Flotation of the as-received coarse powder reduced the graphite content from 0.14 to 0.04% (Table 12).
c) Flotation after ball milling the as-received powder to a smaller particle size did not remove more graphite. The ratio of low graphite containing tailings to higher graphite containing overflows was less favorable than with the coarser material (Table 13).
d) A repeated flotation after intermediate ball milling of the first flotation tailings reduced the graphite content to 0.02% (Table 14).
e) Overflows and tailings showed distinct differences with regard to particle sizes, which were not anticipated.
f) The oxygen content was not affected by flotation.

4. Additions of various reagents into the flotation cell in order to increase selectivity of the separation did not improve the procedure. It was, however, possible to work out a procedure by which the carry-over of TiC into the overflow was kept to a minimum, and the end point could be determined fairly well. This procedure consisted in running the flotation with the cell only half filled and for as long a time as necessary until the froth bubbles had only a grayish film.

Discussion

It is generally claimed that a low graphite containing TiC is superior to one with high graphite content. The flotation experiments were

TABLE 12

FLOTATION OF AS-RECEIVED TiC

	Weight Grams	Oxygen %	Graphite %	Particle Size Microns
As received	1000	0.24	0.14	23
Overflow	129	0.27	0.80	18.4
Tailings	834	0.22	0.04	27

TABLE 13

FLOTATION OF BALL MILLED TiC

	Weight Grams	Oxygen %	Graphite %	Particle Size Microns
As ball milled	500	0.69	0.14	2.5
Overflow	139	0.74	0.32	1.6
Tailings	351	0.65	0.06	3.5

TABLE 14

FLOTATION OF BALL MILLED TAILINGS OF A FORMER FLOTATION (TABLE 12)

	Weight Grams	Oxygen %	Graphite %	Particle Size Microns
Original	500	0.69	0.04	—
Overflow	130	0.70	0.06	1.9
Tailings	305	0.68	0.02	2.4

undertaken mainly in order to upgrade as-received powders. The flotation fractions, which should vary chemically from each other only in the graphite content, were used for investigations on the effect of varying amounts of graphite. The results of the experiments showed, however, that flotation fractions also vary as to their particle sizes. Investigations of both these factors, free graphite content and particle size, were carried out and are described in their respective chapters.

SECTION II

PROPERTIES OF UNBONDED TITANIUM CARBIDE BARS

A. Hot Pressing of Unbonded Titanium Carbide

Introduction

Hot pressing of binder free titanium carbide was undertaken in order to investigate the influence of production procedure, particle size and impurities on maximum obtainable density.

Experiments

Bars of 1-1/2 in. x 1/4 in. x 1/4 in. were hot pressed by the following procedure:

1. 6.5 to 8 grams of TiC powder were pressed cold in a graphite die with a pressure of 1 to 1.5 tsi.
2. With the pressure still on, the specimen was brought to the desired temperature by resistance heating (1500° to 2200°C).
3. When the desired temperature was reached, the current was either shut off immediately or left on for a certain length of time (up to one minute).
4. The pressure was released when the temperature had dropped to 1700°C after the current was shut off. (Temperatures were measured on the outside of the die wall by a Rayo-tube and recorded by a Leeds & Northrup Speedomax Recorder).
5. The specimen was either cooled rapidly in the graphite die between the water-cooled copper electrodes or removed while still glowing and allowed to cool slowly in air.

The variations in pressing procedure had to be used in order to obtain optimum densities with the different powders.

Results

Reference is made to WADC Technical Report 54-13, dated February 1954, which contains a tabulation of all powders treated in the above way

and the densities obtained. The following is a short summary of the results obtained with Kennametal, Metallwerk Plansee and Metro-Cutanit powders.

The following factors were found to increase densification:

a) decrease in particle size
b) addition of free carbon up to 1%
c) leaching of the TiC powder with hydrochloric acid or acetic acid
d) ball milling in a tungsten carbide mill.

Factors which had a detrimental influence were:

a) addition of more than 1% WC in the form of a -100 mesh size powder before ball milling
b) additions of TiN or TiO.

The densification of Norton powder was generally very poor. The highest density obtained was 95% with a flotation fraction containing 8.3% free carbon and an average particle size below 1 micron.

Conclusions

Unbonded titanium carbide specimens of various densities were obtainable by the above described hot pressing procedure. One hundred per cent dense pieces could only be produced if the titanium carbide powder had an average particle size of not more than about 1 micron and was of high purity.

B. Electrical Resistivity Measurements

The electrical resistivity of unbonded hot pressed titanium carbide bars was measured with the help of a specially designed bar holder which made it possible to immerse the investigated specimen in a constant temperature bath (Fig. 5). Measurements were made at various temperatures and the influence of particle size, free carbon content and impurities was investigated.

The following results were obtained:

1. Differences in particle size of a powder did not influence resistivity.
2. Presence of an excess of free carbon before hot pressing, which was investigated in a range up to 1%, also did not influence resistivity.
3. Leaching of a powder with hydrochloric acid, and thus removing oxide films and iron picked up during ball milling, lowered the resistivity by about 10 microhm-cm at all densities.
4. The resistivity decreased, as expected, with increasing density. The lowest resistivity measured with all investigated powders on bars of about 95% of theoretical density was in the vicinity of 85 microhm-cm.

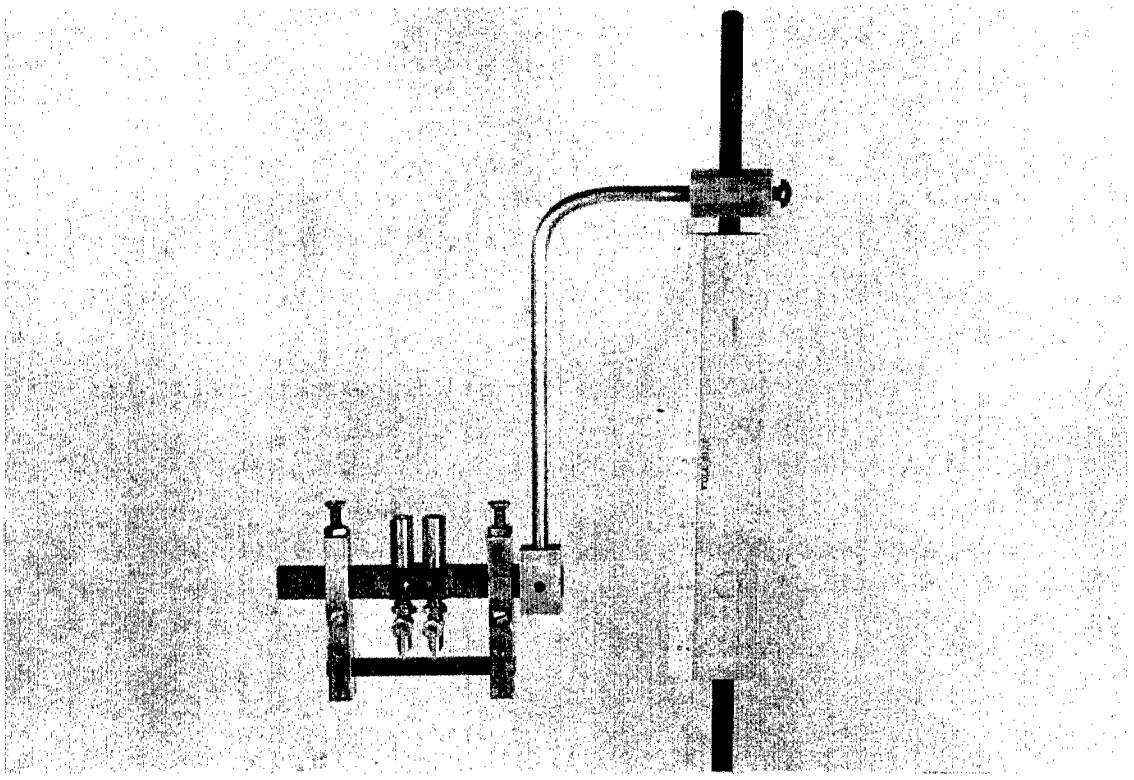


Fig. 5 Specimen Holder for Electrical Resistivity Measurement

In the belief that the thermal coefficient of electrical resistivity might be more sensitive to the influence of impurities than the resistivity itself, this coefficient was determined for a number of specimens between -60° and +100°C. The results were not conclusive. The hope that resistivity measurements could be used as quality control test for different powders could not be realized.

C. Corrosion Study

Experiments

The corrosion studies were carried out in moving air which was purified by filtering, drying, and removing the CO_2 in a larger tower filled with Caroxite, an indicating CO_2 absorbent (Fisher Scientific Co.). The specimen, supported by an Alundum boat, was heated to 1000°C in a small tube furnace. The air flow was kept at about 2 cu. ft. per hour. The tube diameter was 1.5 in.

After leaving the furnace the gas stream passed through two absorption bulbs filled with Ascarite. The experiment was interrupted after certain time intervals and the specimen taken out of the furnace, cooled in a desiccator and weighed. Both absorption bulbs were also weighed. Normally one Ascarite bulb was able to absorb all of the CO_2 formed; the weight of the second bulb only started to increase when the first was exhausted. When this happened, both bulbs were refilled with fresh Ascarite. The following four unbonded TiC specimens were hot pressed from Kennametal powder and submitted to the corrosion test:

Specimen 1 - Powder ball milled in steel mill to 1.3 microns, iron content after this operation 0.94%, hot pressed density 98.4%.
Specimen 2 - Powder ball milled in steel mill to the same particle size as 1, and leached with hydrochloric acid, which reduced the iron content to 0.12%, hot pressed density 74.2%.
Specimen 3 - Same as 1, hot pressed density 74.2%.
Specimen 4 - 10% WC added to powder, mixture ball milled to 1.2 microns and leached with hydrochloric acid. The iron content was 0.12%, hot pressed density 98.4%.

At the end of each experiment, the coating was peeled off the specimen as far as possible. It came off in layers which were X-rayed separately.

Results

Table 15 gives the weight gain in mg/cm^2 of surface area of the four specimens in the column "Observed". The figures in column "Calculated" were derived from the amount of CO_2 absorbed by the Ascarite bulbs assuming that the oxidation of TiC produced exclusively TiO_2.

X-ray diffraction analyses of the peeled off layers had the following results:

TABLE 15

CORROSION STUDY

Specimen No.	Powder/Specimen No.	Density %	Time Hours	Weight Gain - mg/cm^2 Observed	Calculated	Appearance of Coat
1	115A/4	98.4	3	10.73	10.67	Shiny, dark-blue to black, adherent
			6	18.02	17.50	
			11	27.9	27.1	
			76	77.4*)	84.2	
2	115B/2	97.8	3	7.20	6.88	Coarse crystalline, irridescent, reddish-black, not very adherent
			6	11.50	10.7	
			11	16.56	15.68	
			35	27.1	27.3	
			64	34.7	35.6	
3	115A/7	74.2	3	17.88	7.04	Same as first sample, but less adherent
			21	54.2	33.2	
			45	78.4	52.3	
			69	96.8	66.7	
			93	115.7	83.7	
4	129/1	98.4	3	2.61		Uniform yellowish-gray, fairly adherent, starting Maltese cross
			6	4.89		
			11	9.31		
			30	19.9		

*) Specimen stuck to boat

For specimens 1 and 2, the outer layers showed only the presence of rutile, highly oriented, and probably a small amount of orthorhombic TiO_2 (brookite). The inner layers consisted essentially also of rutile, randomly oriented. There were in both layers very weak unidentified lines probably of some lower oxides of titanium. No indication of the presence of either TiO or TiC could be found. Fig. 6, a photomicrograph of specimen 1 (Table 15) shows the layer formation of the oxide coating.

For specimen 3 the coating consisted of alternating gray and black layers, the innermost layer, which was very small and fairly adherent, was yellowish gray. The X-ray diffraction pattern of the uppermost coating showed TiO_2 (rutile) and a minor unidentified pattern of probably some lower titanium oxide. Deeper situated layers were identified as TiO_2 and TiC, no TiO could be found.

Specimen 4 showed a more uniform coherent coating than the three other specimens. The X-ray diffraction pattern was also that of rutile, with no indication of the presence of TiO or TiC. There were several minor peaks which appeared to indicate the presence of a small amount of WO_3 and also possibly some WO_2. Fig. 7, a photomicrograph of specimen 4, shows the greater uniformity of the oxide layer.

The coating of specimen 2, which peeled off easily, had the following analysis:

Ti	60.5%
C_{total}	0.08%
N_2	0.1%

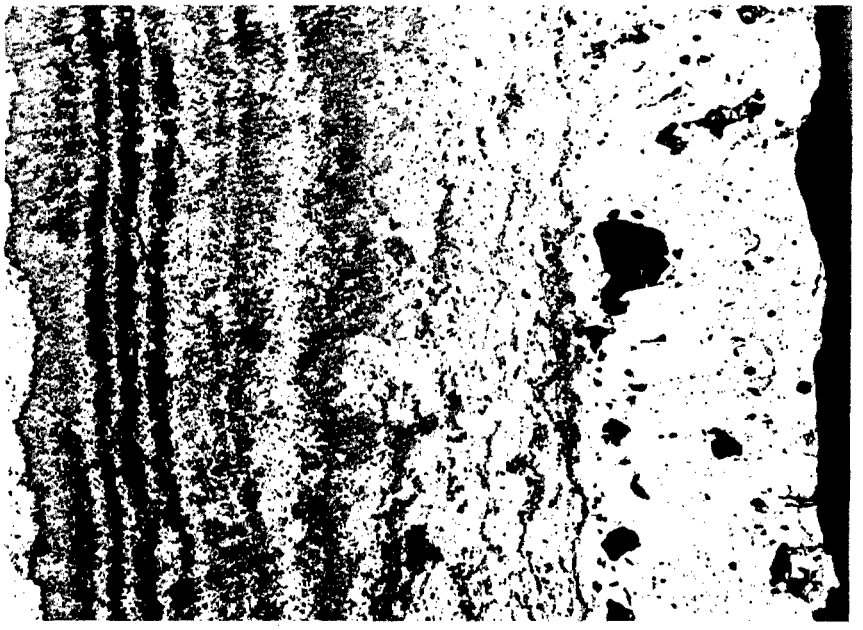
TiC_2 has a stoichometric composition of 60% Ti and 40% O_2. Due to the high oxygen content, no direct oxygen determination could be made.

Conclusions

X-ray diffraction as well as chemical analyses showed that the only corrosion product of a dense piece of pure TiC was TiO_2. The assumption made above for the "Calculated" figures were, therefore, justified. The actual figures given in Table 15 under "Observed" and "Calculated" are similar for specimens 1 and 2. The procedure can, therefore, be used to follow the corrosion of a dense piece of pure TiC in air at elevated temperature by determining the amount of CO_2 evolved. This simple relationship did not hold true for a less dense piece (specimen 3) or for a dense piece which contained WC (specimen 4). The "Calculated" values were lower than the "Observed" values for specimen 3, a fact which could not be explained, as the X-ray diffraction analysis did not reveal any other compounds than TiO_2 and TiC. Oxidation of a TiC/WC piece was complicated by the fact that tungstic oxide was partly volatilized and that the oxidation of the components TiC and WC did not necessarily progress with the same speed. "Calculated" figures of this case have therefore been omitted in Table 15.

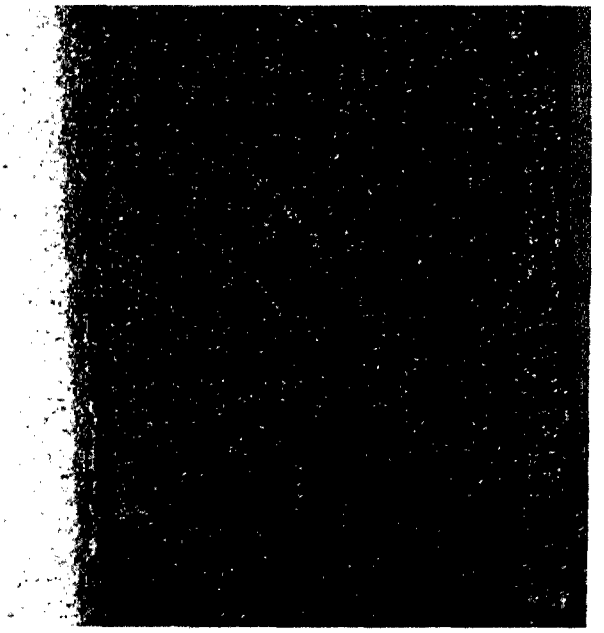
Comparing the "Observed" figures of Table 15, it can be concluded:

1. Purification of a powder by leaching decreased the corrosion rate of the hot pressed dense piece.



TiC Inner Layer Outer Layer 100 X

Figure 6. TiC after 76 hours in air at 1000° C



TiC Oxide Layer 100 X

Figure 7. 90/10 TiC/WC after 98 hours in air at 1000° C

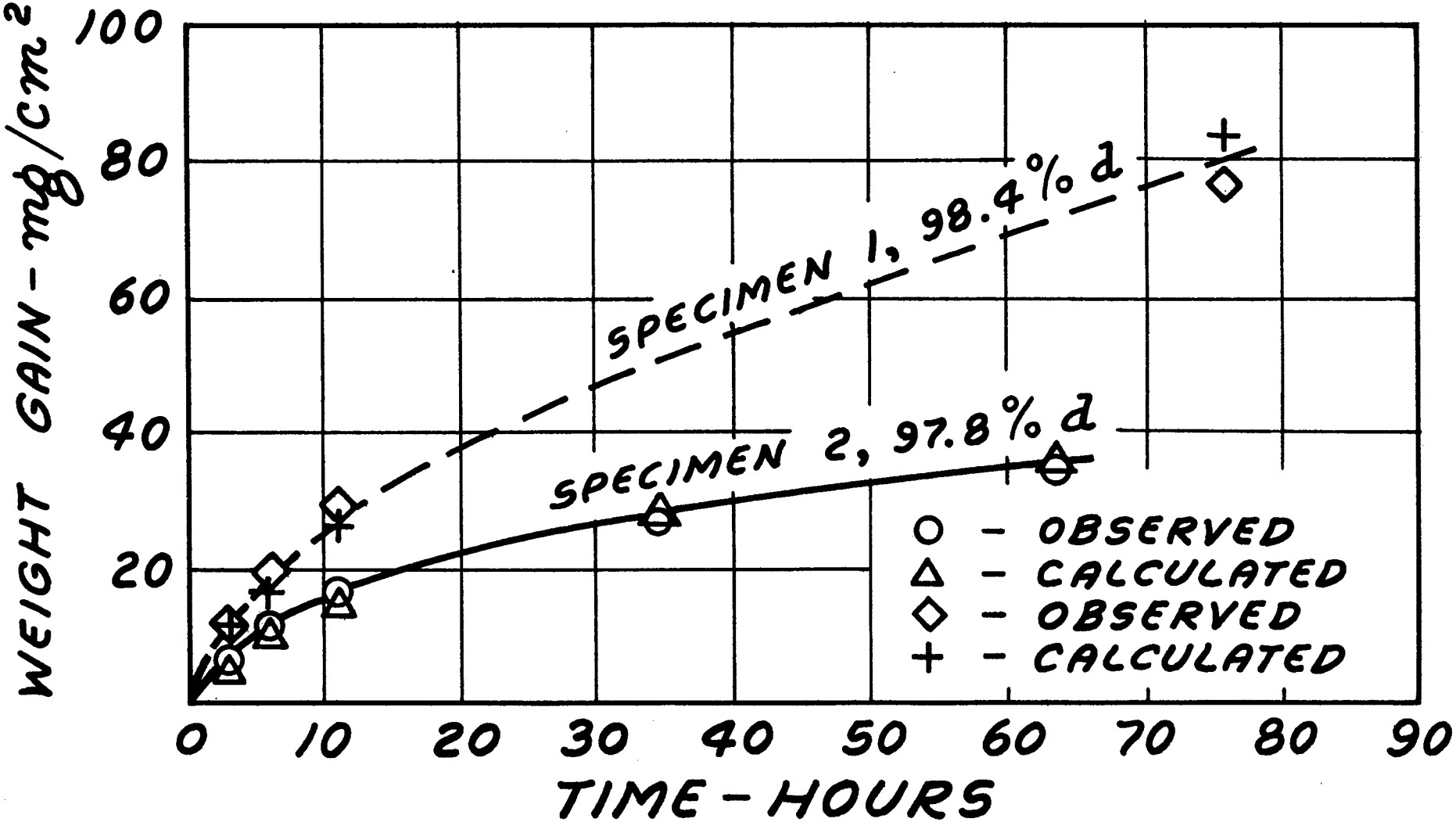


FIG. 8 CORROSION OF TiC IN MOVING AIR
WEIGHT GAIN VS. TIME

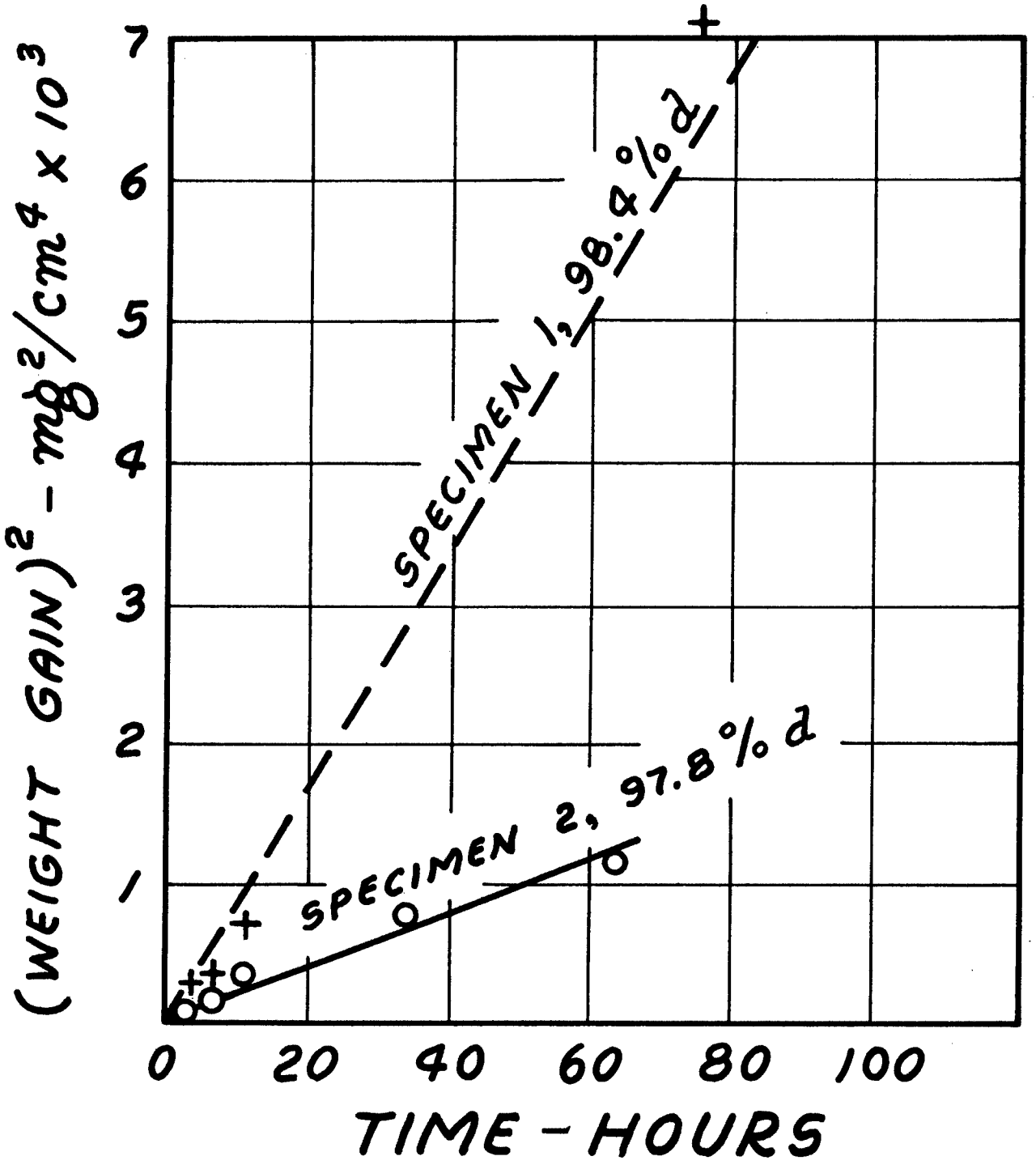


FIG. 9 CORROSION OF TiC IN MOVING AIR
(WEIGHT GAIN)^2 VS. TIME

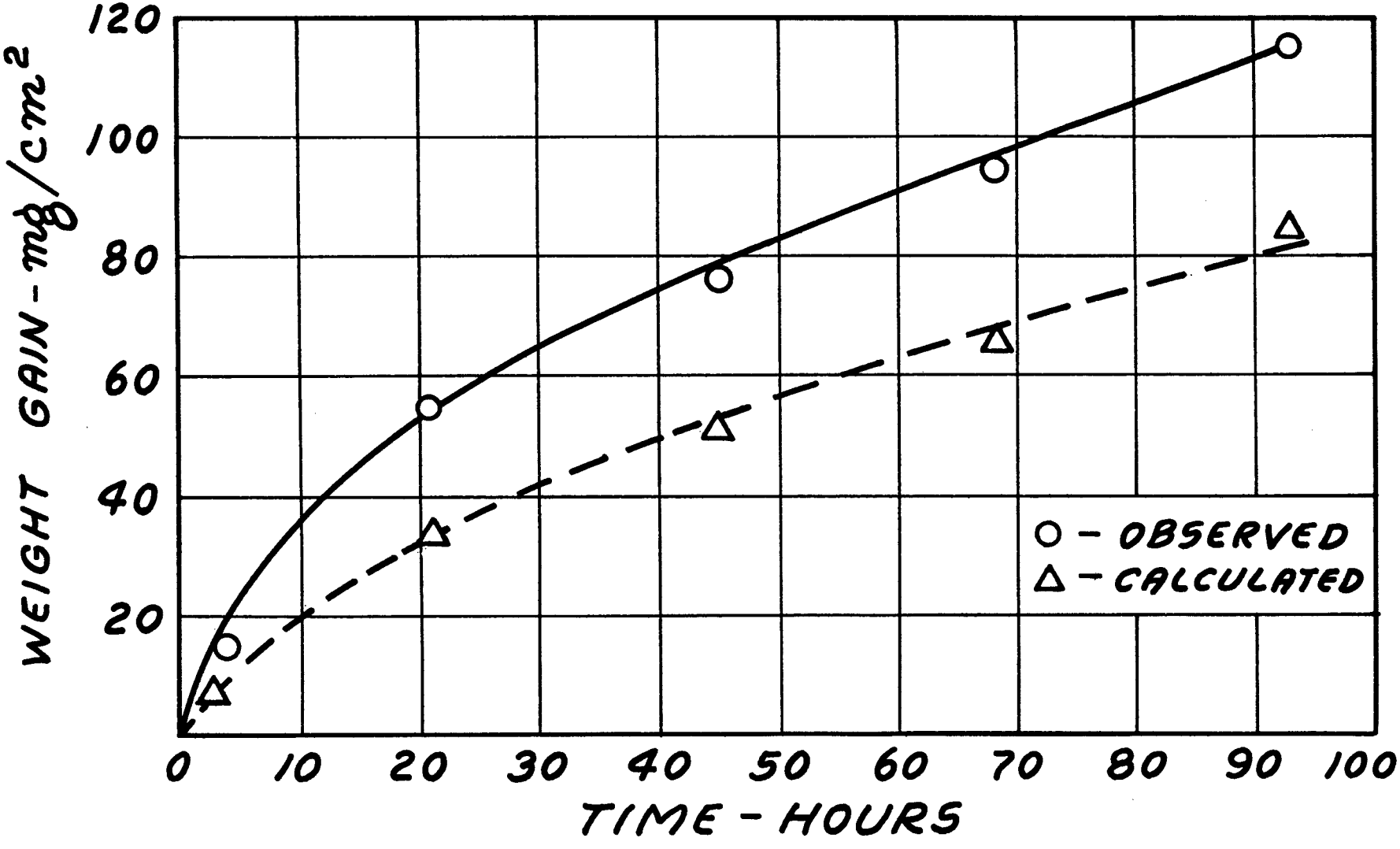


FIG. 10 CORROSION OF POROUS TiC IN MOVING AIR
WEIGHT GAIN VS. TIME
SPECIMEN 3, 74.2 % d

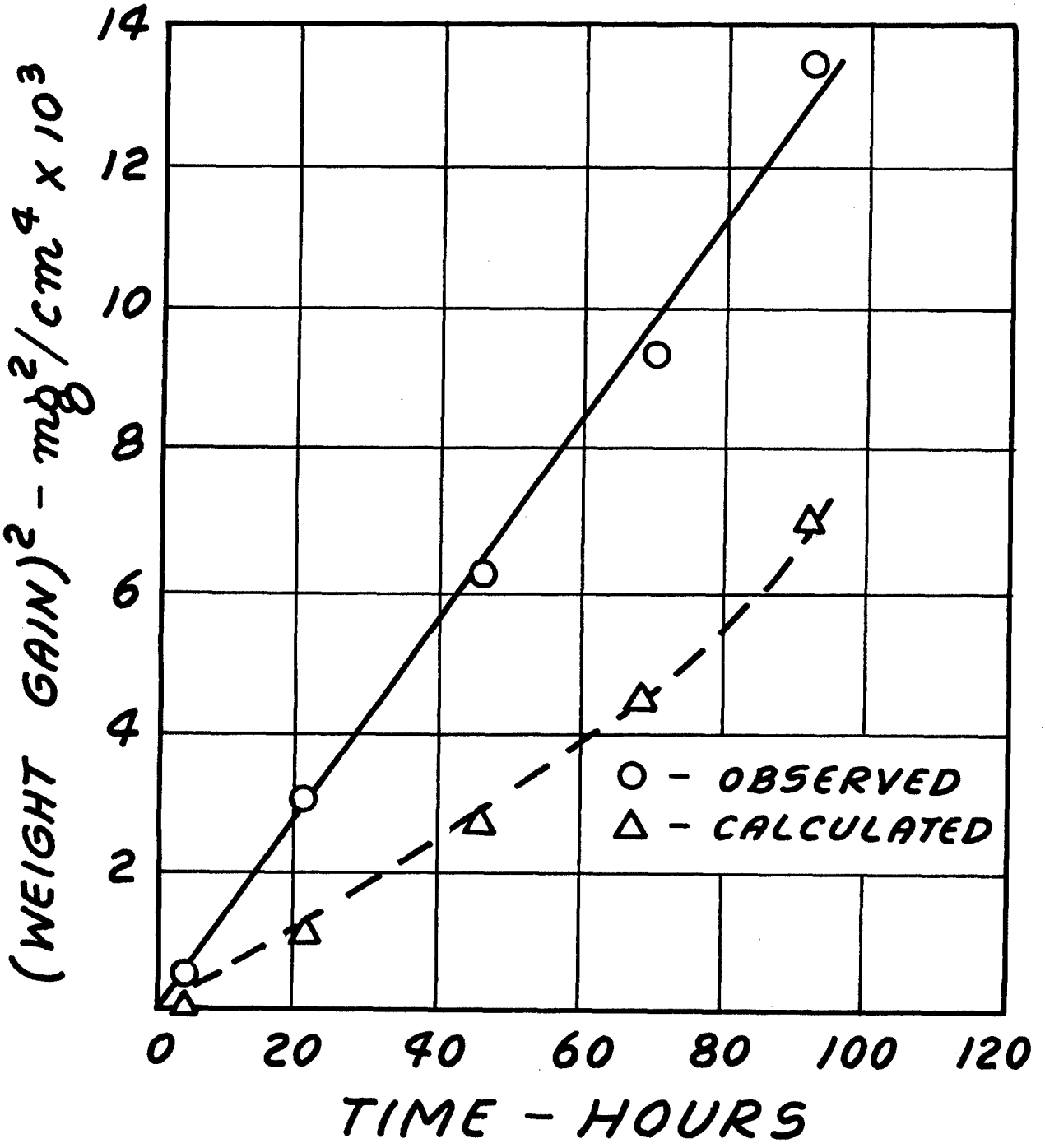


FIG. 11 CORROSION OF POROUS TiC IN MOVING AIR
(WEIGHT GAIN)^2 VS. TIME
SPECIMEN 3, 74.2% d

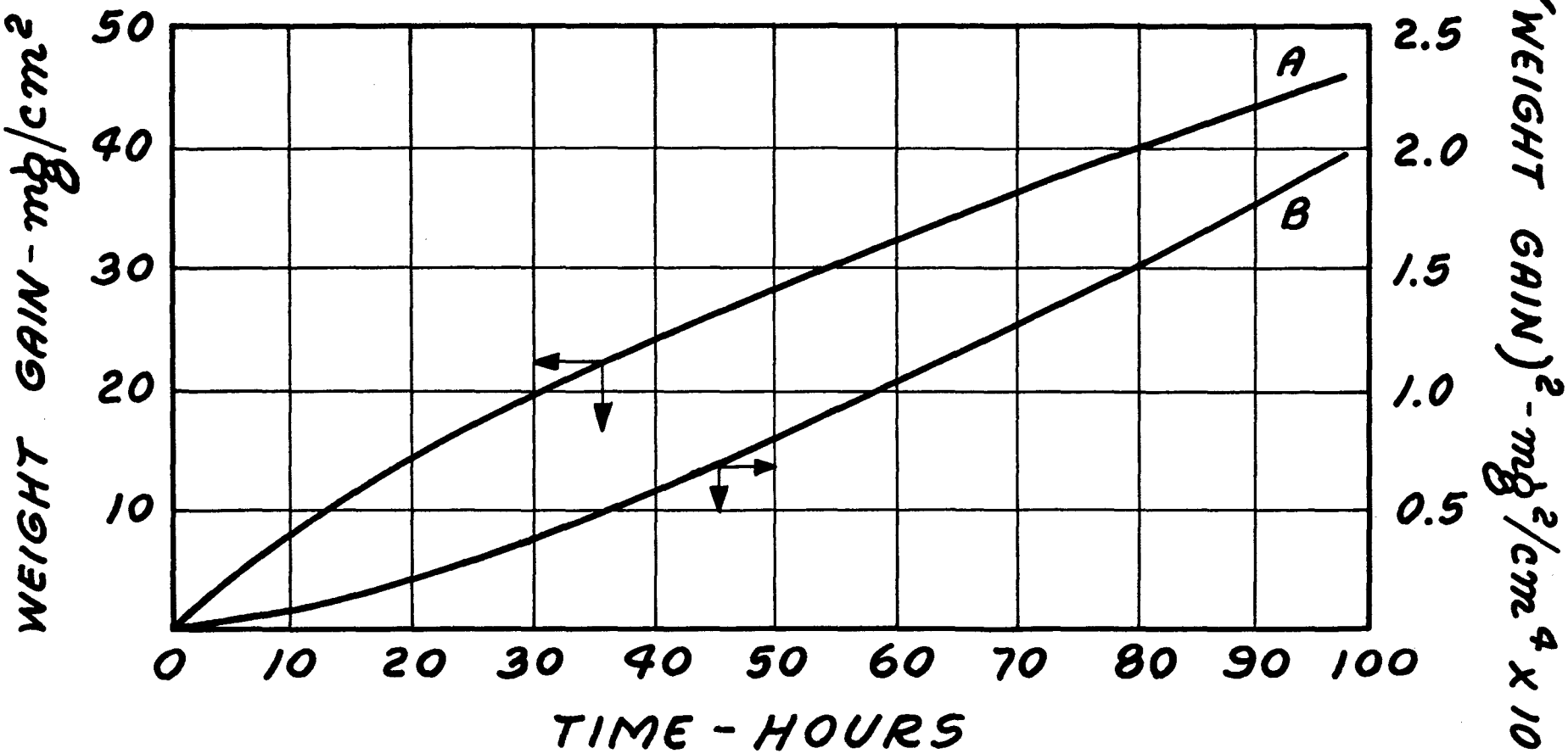


FIG. 12 CORROSION OF 90/10 TiC WC IN MOVING AIR
SPECIMEN 4, 98.4 % d

2. Decrease of density increased corrosion rate, as expected, and also changed the corrosion mechanism.
3. The influence of the presence of WC was complicated by the fact that WO_3 was formed which partly volatilized.

In Fig. 8 the weight gain per surface area of specimen 1 and 2 was plotted against time, and in Fig. 9 the square of the weight gain of the same samples was plotted against time. The curves show a truly parabolic relationship between weight gain and exposure time. It is known that such a relationship occurs by diffusion through an ever increasing thickness of oxide. Diffusion through the growing oxide layer determines the rate of reaction.

Figs. 10 and 11 show similar plots for the porous specimen 3. The curves of "Observed" and "Calculated" values are not identical as is the case with dense specimens; but there is an indication that the ratio of "Observed" over "Calculated" values, Table 15, becomes constant. If the values after 3 hours are disregarded, the ratio "Observed" over "Calculated" values is 1.4 to 1.6. If further experiments would establish that this ratio is only a function of the density of the investigated pieces, this method would possibly enable one to follow the oxidation process for porous pieces by weighing the CO_2 evolved.

In Fig. 12 weight gain (A) and square of weight gain (B) of specimen 4 were plotted against time. Due to the volatilization of one oxidation product (WO_3), the weight gain vs. time curve in this case is not truly parabolic.

SECTION III

INFILTRATION OF TITANIUM CARBIDE SKELETONS

Introduction

The aim of these experiments was twofold: 1) to investigate the factors which influence the infiltration of porous titanium carbide compacts with liquid metal, and 2) to find out if a correlation exists between the infiltrability of binder-free hot pressed bars and the physical properties of binder containing hot pressed pieces of the same material. A positive answer to the second question would make it possible to predict the physical properties of a metal-bonded TiC end-product and to select materials for certain requirements by investigating the ability to infiltrate a TiC skeleton.

Meerson and co-workers[7] used the infiltration of TiC compacts with cobalt in an attempt to distinquish between various grades of titanium carbides. They reported that pure TiC, produced by reduction of titanium oxide with lampblack in vacuum and hot pressed into bars, infiltrated com-

pletely, while bars pressed from less pure commercial materials infiltrated only partly or not at all. Their explanation for this occurrence was that oxygen was present in commercial powders as TiO in solid solution with TiC. At elevated temperatures this oxygen reacted with carbon, producing CO which caused the formation of a porous core and so prevented complete infiltration. As this core formation also took place when TiC was used as an addition to WC, infiltration experiments could reveal, in Meerson's opinion, whether or not a certain grade of titanium carbide could be used for the production of sound WC-TiC compacts.

Fig. 13 was taken from Meerson's publication. Numbers 1 and 2 were bars of a "normal commercial titanium carbide" with about 17% combined and 1% free carbon and 3% oxygen. They infiltrated only partly. Number 4 was a bar of titanium carbide which caused core formation. The analysis of this material, according to Meerson, was 17.2% combined and 1% free carbon and 3.25% oxygen. It did not infiltrate at all. The completely infiltrated bar No. 3 was vacuum produced TiC, with 19.2% combined and 0.4% free carbon and 1% oxygen. Meerson calculated all oxygen percentages by difference and did not determine nitrogen and other impurities. Densities of bars are not mentioned in the publication.

Experiments

Infiltration experiments were carried out in a way very similar to that of Meerson. Compacts 1-1/2 in. x 1/4 in. x 1/4 in. were hot pressed from different ball milled powders to densities varying between 60 and 85% of theoretical density. The porous bars were placed in small graphite crucibles containing the infiltrant in the form of a powder. The amount of infiltrant was in slight excess of that required to completely infiltrate the pore space. Several of the smaller crucibles were then inserted in a larger insulated graphite crucible. The temperature of this assembly was rapidly raised by high frequency induction heating to 1550°C and held for one hour. All experiments were carried out in a controlled atmosphere. After cooling, the infiltrated bars were ground down to half their initial thickness to measure the depth of infiltration.

By using different powders and ball mills and varying ball milling and pressing procedures as well as infiltrants and atmospheres, the influences of the following factors were investigated:

1) Production procedure of TiC
2) Particle size of the TiC powder before hot pressing
3) Density of the hot pressed TiC skeleton
4) Presence of free carbon in the TiC powder
5) Presence of TiN and iron
6) Oxygen content of TiC
7) Presence of WC in the TiC powder
8) Gas atmosphere during infiltration
9) Nickel or cobalt as infiltrants

To find out whether infiltration can completely fill out the pore space of a porous bar, the center part of a well infiltrated bar was cut out

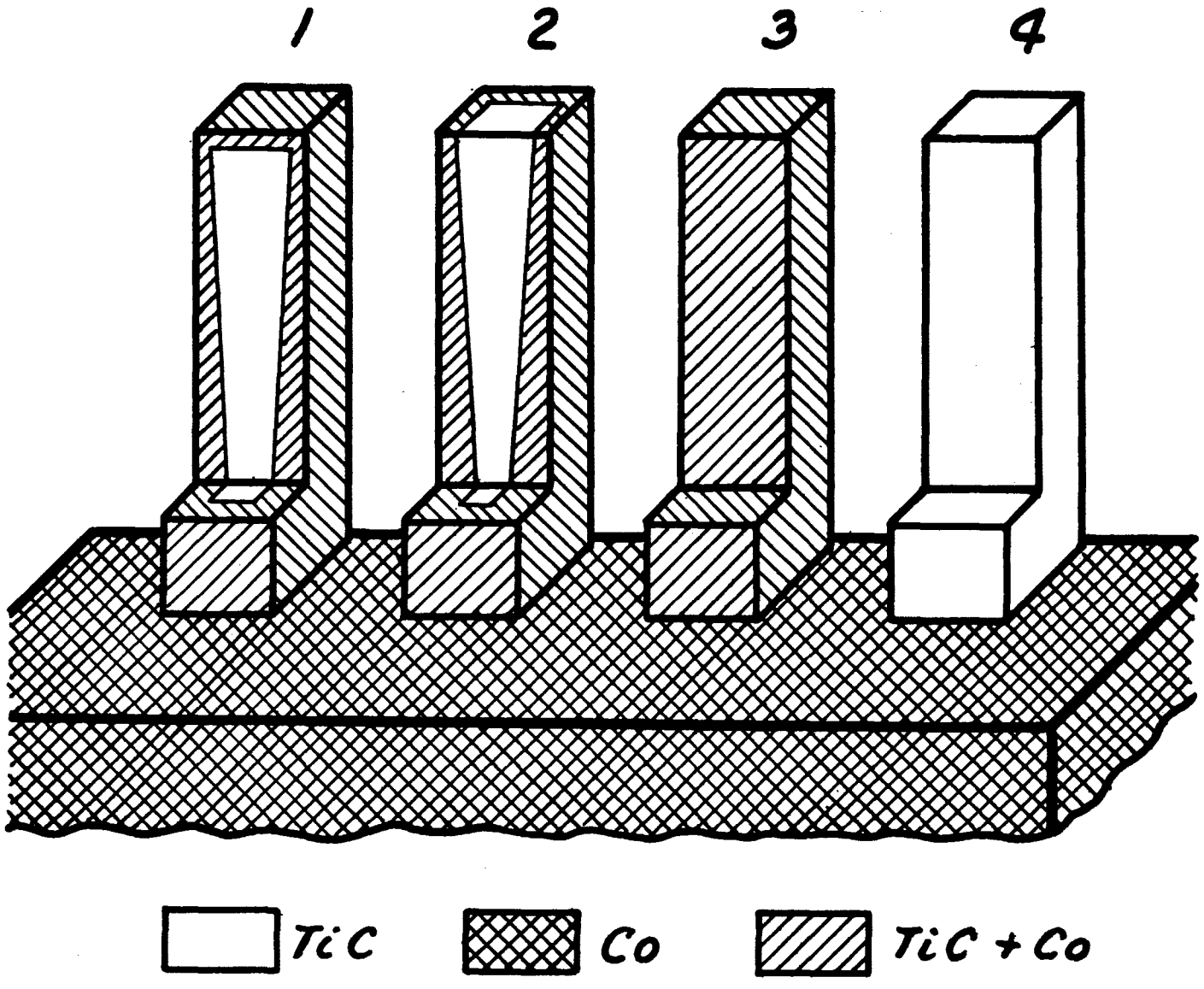


FIG. 13 INFILTRATED BARS ACCORDING TO MEERSON

and its density determined pycnometrically. This piece was then crushed and chemically analyzed. The result of this analysis was used for a calculation of the density assuming that the law of mixtures applied.

Results

1. Influence of Powder Production - The production procedure of a titanium carbide had no direct influence on infiltrability. All investigated materials could be infiltrated if the proper conditions for infiltration were maintained. Some powders might be in these conditions already when received (see under "Discussion"), others might require a treatment to bring these conditions about. The conditioning treatment could consist either in a ball milling procedure or in the use of a special atmosphere during infiltration, both of which increased the wetting properties of the individual particles.

2. Influence of Particle Size - The particle size of the ball milled powder had an influence on the ability of a hot pressed bar to infiltrate, the smaller the particle size the better the infiltrability under otherwise equal conditions. This can have two reasons: (1) the height of the rise of the liquid in a capillary is inversely proportional to the radius of the capillary. The smaller the particle size of a powder, the smaller will be the radii and the larger will be the number of capillaries after hot pressing to a given density. (2) Ball milling for a longer time to obtain a smaller particle size might give the particles the proper surface conditioning necessary for infiltration.

3. Influence of Density - The density of a hot pressed bar had a decisive influence on its infiltrability. Under otherwise equal conditions, there was a density range for each powder in which complete infiltration could be obtained. Depending upon other conditions, this range was narrower or wider. It was always between 60 and 85% of theoretical density, and if surface conditions for optimum infiltrability were properly attained, bars covering this whole range of density could be infiltrated giving a wide variation of carbide to binder ratio for the final product.

4. Influence of Free Carbon - The presence of free carbon, when it was added before ball milling, had a detrimental influence insofar as small amounts (up to 1%) narrowed the density range of infiltrability. Larger amounts prevented infiltration completely. This is believed to be due to a coating of the particles with graphite, which lowered their wettability. Bars hot pressed from various flotation fractions of Norton TiC, containing from 0.25 to 12% free carbon, could not be infiltrated in an atmosphere of dry hydrogen even when the particle size was below 1 micron. A powder which could be infiltrated in a dry hydrogen atmosphere lost its infiltrability after it was mixed with 0.5% carbon by ball milling. In a wet hydrogen atmosphere the TiC-carbon mixture could be partly infiltrated. After ball milling with water, the same mixture could be completely infiltrated in an argon atmosphere. The same was found to be true for the flotation fractions of the Norton powder. The proper atmosphere or conditioning during ball milling can remedy the detrimental effect of free carbon.

5. Influence of TiN and Iron - An addition of 10% TiN to TiC before ball milling did not affect infiltrability in any way. X-ray investigation showed complete solid solutions of the two components after hot pressing.

Iron in amounts of up to 1%, picked up during ball milling in a steel mill, also did not affect infiltration.

6. Influence of Oxygen - In order to substantiate Meerson's claim that the presence of TiC/TiO solid solution was responsible for infiltration failures, up to 20% TiO were added to TiC before ball milling. X-ray analyses established complete solid solution after hot pressing. The powder mixture 80/20 TiC/TiO contained 5.55% oxygen which was reduced during hot pressing to 4.07%. In the most adverse atmosphere used in these investigations -- dry hydrogen --, bars with this oxygen content could be infiltrated completely. The oxygen content did not change during infiltration according to chemical analyses, taking the amount of infiltrated cobalt into consideration.

The addition of 2% TiO_2 to TiC powder before ball milling improved infiltrability in dry hydrogen as well as in argon.

It has been pointed out before and substantiated by chemical analyses that ball milling in air, and more so ball milling in water or alcohol, caused an oxygen pickup in the form of a TiO_2 film around the individual particles. At least part of this film was retained after hot pressing. The infiltrability of bars pressed from powders which had acquired this film during ball milling was superior to those without it and also to those of which the film had been stripped by a hydrochloric acid leach prior to hot pressing.

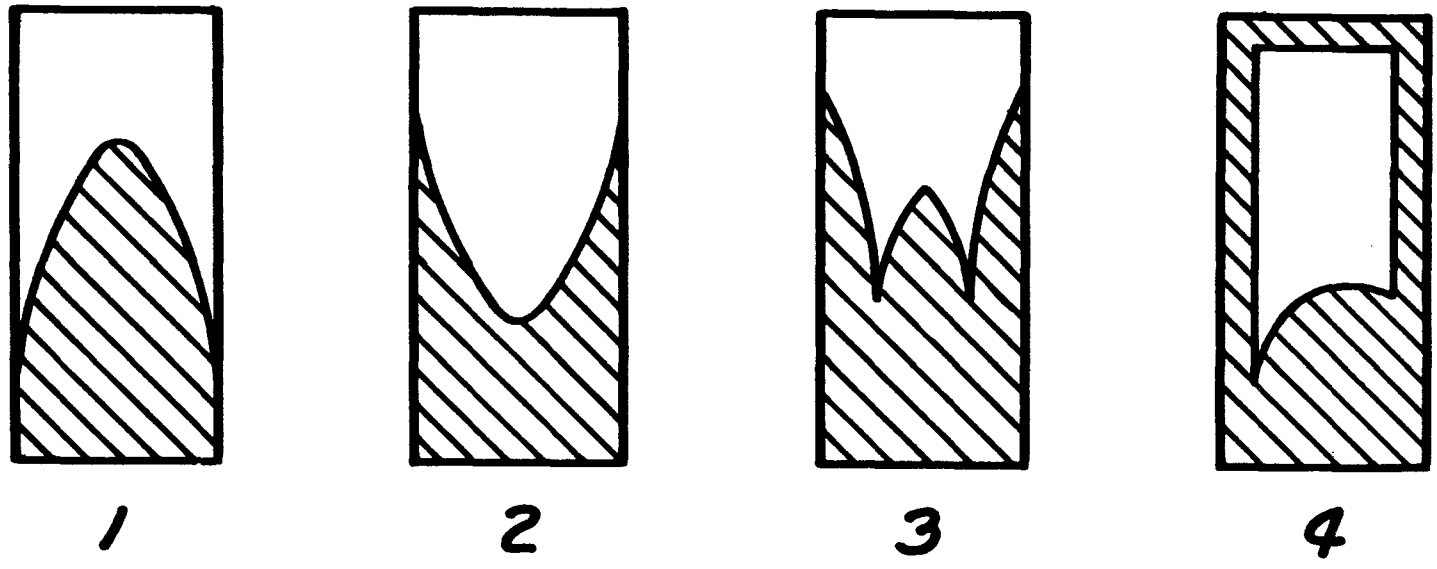
7. Influence of WC - Contrary to the iron, picked up from the steel mill, which did not affect infiltrability, the WC picked up during ball milling in a tungsten carbide mill had a beneficial effect. The same effect was reached by an addition of up to 10% WC to TiC before ball milling in a steel mill. The detrimental effect of a hydrochloric acid leach was neutralized by the WC addition and good infiltrability was preserved.

8. Influence of Atmosphere - A strongly reducing atmosphere of dry hydrogen proved detrimental to infiltration. Only if particle size and density conditions were very favorable, so that complete infiltration could occur before reduction of the beneficial oxide film, could infiltration run to completion. If, however, the oxide film around the particles had been reduced before infiltration was complete, partly infiltrated bars resulted, showing an infiltration pattern similar to Fig. 14-1.

A slightly oxidizing atmosphere which occurred when bottle hydrogen was not properly dried proved a favorable but not too well controllable atmosphere. The incompletely infiltrated bars in this atmosphere showed patterns similar to Fig. 14-2.

The "neutral" argon atmosphere proved in fact to be slightly reducing probably due to the presence of CO in the infiltration furnace. But under otherwise favorable conditions, reduction of the oxide film was so slow that complete infiltration could be accomplished before reduction. Bars incompletely infiltrated in an argon atmosphere, due to unfavorable density or other conditions, showed patterns similar to Fig. 14-1 or -3.

An atmosphere of wet hydrogen, produced by bubbling bottle hydrogen through water, was found to be highly oxidizing. Hardly any bars could be completely infiltrated in this atmosphere, but almost all bars infiltrated partly, showing patterns similar to Fig. 14-4.



BASIC PATTERNS OF INCOMPLETELY INFILTRATED BARS

FIG. 14

Hot pressed titanium carbide bars were run along in infiltration runs without the addition of an infiltrant. Oxygen analyses of these "blanks" before and after the infiltration run revealed the character of the atmosphere during the run. In a wet or not properly dried hydrogen atmosphere the oxygen content of these blanks increased, in a well dried hydrogen atmosphere it decreased and in an argon atmosphere it did not change or it decreased very slightly.

9. Influence of Infiltrant - Both nickel and cobalt were used as infiltrants. Under the same conditions both metals behaved entirely alike as far as infiltration was concerned. Photomicrographs of infiltrated bars showed, however, a characteristic difference; cobalt infiltrated bars had almost completely rounded titanium carbide particles, while in nickel infiltrated bars the particles stayed angular with only some rounding of edges taking place. There was considerable grain growth in both cases (see Fig. 15).

10. Density of an Infiltrated Bar - The pycnometer density of the innermost part of a well infiltrated bar was 5.36 g/cc. When the density was calculated from the chemical analysis, using the law of mixtures, the value obtained was 5.35 g/cc (Table 16, column 3).

TABLE 16

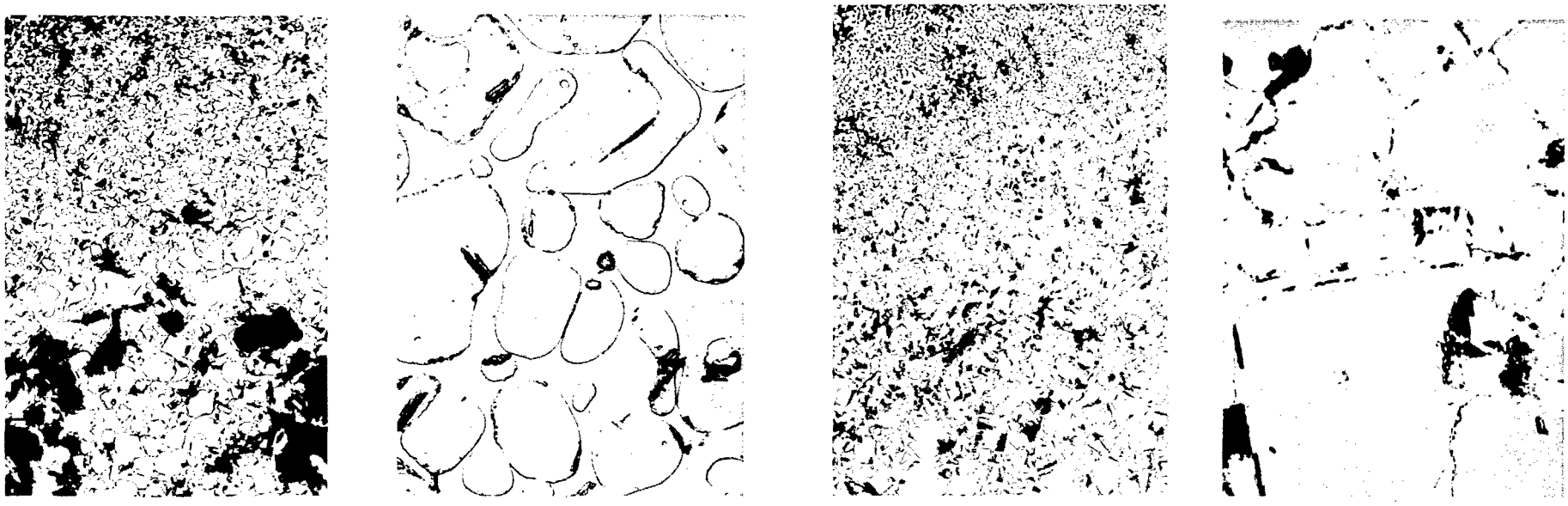
ANALYSES OF AN INFILTRATED BAR AND THE ORIGINAL POWDER

(Kennametal Powder)

	As Received	As Ball Milled	Infiltrated
Ti	79.7%	78.0%	61.3%
C_{comb}	19.4	18.5	14.8
C_{free}	0.21	0.85	1.3
Fe	0.06	0.94	0.73
O_2	0.10	1.74	0.01
N_2	0.15	0.30	—
Co	—	—	22.3
Total	99.62	100.33	100.44
$\frac{C_{comb}}{Ti + C_{comb}}$	19.6	19.2	19.4

Discussion

Infiltrability of a porous compact is influenced mainly by two factors: 1) porosity and pore distribution, and 2) condition of the particle surface. It is obvious that a network of interconnected pores is necessary in order to obtain 100% density by infiltration. For this reason, densities of titanium carbide skeletons to be infiltrated should not be higher than about 85%. On the other hand, densities should not be too low. Otherwise the radii of the capillaries formed by the interconnected pores might be so



X200 a | X1000 b | X200 c | X1000 d

Ball Milled in Steel Mill (1.9 Microns), Hot Pressed to 78% Density

Cobalt Infiltrated | Nickel Infiltrated

Fig. 15 Infiltrated Titanium Carbide Bars
(Titanium Alloy)

large that the capillary forces are too weak to raise the liquid binder sufficiently for complete infiltration. Low density of the compact also weakens the skeleton, and "sagging" of the bar may be the consequence.

The second factor is wettability of the carbide skeleton which is a function of the surface condition of the individual particles. The foregoing experiments and their results have shown that a slight surface oxidation of the carbide particles to TiO_2 is essential for complete infiltration. The liquid infiltrant wets the TiO_2 film well without reacting with it. The carbon dissolved in the infiltrant from the crucible reacts with the TiO_2 forming either TiC or TiO which in turn forms a solid solution with TiC. The formation of the beneficial oxide film takes place during ball milling in air and to a higher extent during ball milling in water or alcohol. If this oxide film is removed, by leaching the ball milled powder with hydrochloric acid, infiltration is inhibited. Leaching with acetic acid has no effect on infiltration as this acid does not remove the oxide film. It was found that ball milling to a very fine particle size could overcome the effect of the hydrochloric acid leach. The possible reasons for this are the formation of finer capillaries during hot pressing and an unavoidable partial re-oxidation of the very fine particles during drying. One particular powder, for instance, was ball milled to 2.3 microns and leached with hydrochloric acid. It had an oxygen analysis of 0.07%. When the same powder was ball milled to 1.5 microns and leached its oxygen content was 0.46%.

Another way to cause the formation of an oxide film was ball milling of the carbide with the addition of 2% TiO_2. The oxide coated the individual particles well and a powder otherwise not infiltrable infiltrated well when treated in this way.

A third procedure to create a TiO_2 film was to carry out the infiltration in an oxidizing atmosphere produced by bubbling hydrogen through water before introducing it into the infiltration furnace. No complete infiltration could be obtained in this way but the pattern presented by partly infiltrated bars was very characteristic (see Fig. 14-4). The oxidation started at the outside of the bar, and infiltration following the oxidation was so rapid that it closed the inside of the bar completely preventing further infiltration.

As a slight oxide film around the individual particles is the main requirement for good infiltration, it is understandable that the production procedure of the TiC has no influence on its infiltrability.

The detrimental effect of free carbon, even if reduced by repeated flotation of the Norton powder to 0.25%, can be explained by the formation of a tenacious coating of graphite around the carbide particles. This coating should react when heated either with the hydrogen of the atmosphere or with an oxide film present. In either case, it would leave an oxide-free surface of low wettability. Only if a thorough oxidation of the particles has taken place by either ball milling in water or by using a wet hydrogen atmosphere during infiltration, is there enough of the oxide film left after reaction with the free carbon that good wettability is maintained.

No explanation can be offered for the beneficial influence which the presence of WC had on infiltration.

Nickel and cobalt infiltrated bars differed only in their microstructure (see Fig. 15). Besides rounding of the TiC particles, the cobalt infiltrated piece showed a large amount of "O" and "C" shaped particles which might have formed in this way: A particular spot of a carbide particle was for one reason or another vulnerable to an attack by the liquid cobalt while the rest of the particle was protected. Through this spot the liquid "invaded" the particle and eroded it from the inside. Cuts through such a particle would present the observed shapes. Fig. 16 presents this reaction in a schematic way giving the carbide particle the form of a cube for simpler presentation.

Fig. 14 shows four basic patterns encountered when incompletely infiltrated bars were machined down to half their original width. Pattern 4 has been discussed above. The other three suggest the following explanations: Pattern 1 was typical for infiltration in a dry hydrogen atmosphere. The atmosphere reduced the oxide film present and this reduction proceeded from the outside of the bar toward the inner part. The inner part could, therefore, be infiltrated to a certain depth before the reduction caught up with the infiltrating liquid and stopped its further progress. Pattern 2 was typical for a slightly oxidizing atmosphere. Oxidizing also proceeded from the outside to the inner part of the bar and the infiltrant following it stopped when capillary forces were in equilibrium with the weight of the infiltrant. Pattern 3 which was observed especially in an argon atmosphere indicates how infiltration proceeded under favorable conditions. The liquid infiltrant did not rise in all the capillaries of the porous bars to the same height simultaneously. The infiltration proceeded fastest at the outer parts of the bar and at the innermost part, while the in-between zone lagged behind. The three zones thus formed were clearly distinguishable in completely infiltrated bars (see Fig. 15, a and c). The outermost zone was very rich in infiltrant, it consisted probably of 80% (by weight) metal with very fine titanium carbide grains embedded in it. Next to it the second zone had probably a 50-50 TiC-binder composition with a little coarser but still fine carbide particles. Both these zones were relatively small. The innermost third zone had large carbide particles completely surrounded by the binder phase (see Fig. 15, b and d). Such a structure, when properly developed, should show interesting physical properties, e.g. a higher impact resistance than TiC with metal binder evenly distributed.

Table 16 gives the analyses of a powder as received, as ball milled in a steel mill to 1.28 microns and of the innermost part of a hot pressed and then infiltrated bar. It shows the relatively high oxygen pickup during ball milling which was completely lost during infiltration and the relatively low cobalt content. The X-ray diffraction pattern of the infiltrated piece showed only the Co and the TiC lines with a lattice parameter of a_o = 4.325 Å. This value indicates that no Co was taken into the TiC lattice.

As it was not the goal of this investigation to develop good physical properties, only a few bars were tested for transverse rupture strengths and impact resistance. The maximum values obtained were 140,000 psi

and 8.5 in.-lbs., respectively.

Conclusions

This investigation has shown that the following factors influence the infiltrability of porous titanium carbide compacts:

1. The particle size of the TiC powder
2. The density of the hot pressed compact
3. The presence of free carbon
4. The surface condition of the titanium carbide particles.

The particle size of the powder and the density of the compact determine the porosity of the carbide skeleton and the radii of the capillaries which have to be filled with the liquid metal. A small average particle size (1 to 3 microns) and densities between 60 and 85% of theoretical density were the optimum conditions for complete infiltration.

The presence of free carbon was detrimental due to its tendency to coat the individual carbide particles and so preventing them from being wet by the liquid infiltrant. The presence of WC, either picked up during ball milling in a tungsten carbide mill or added before ball milling the TiC in a steel mill, had a beneficial influence. The reason for this influence is unknown.

The most important factor was the condition of the surfaces of the individual carbide particles. This condition determines the wettability of the particles. It could be shown that an oxide film covering the surfaces of the individual particles was most desirable because of its good wetting properties. This film could be obtained in three different ways, by ball milling the TiC powder in water or alcohol, by adding a small amount of TiO_2 before ball milling, or by carrying out the infiltration in a slightly oxidizing atmosphere.

The infiltrability of a porous TiC skeleton was found to be independent of the production procedure of the TiC powder, the presence of a small amount of iron, the presence of TiN or TiO in solid solution and the use of nickel or cobalt as infiltrants.

The second aim of this investigation was to find a correlation between physical properties of bonded TiC pieces and the ability to infiltrate a binder-free skeleton of the same material. This aim, which was prompted by Meerson's claim of the detrimental influence of the presence of oxygen, could not be realized. It has been shown that the presence of TiO in solid solution with TiC does not prevent infiltration. An explanation of Meerson's results, however, cannot be given as pertinent data such as ball milling procedure of the powder, preparation of the carbide skeletons and their densities are not known. Meerson mentions that he used hydrogen as a protective atmosphere. From the infiltration patterns of Fig. 13-1 and -2, which are similar to those of Fig. 14-2 and 14-4, it must be concluded that the hydrogen was not dry and the atmosphere slightly oxidizing.

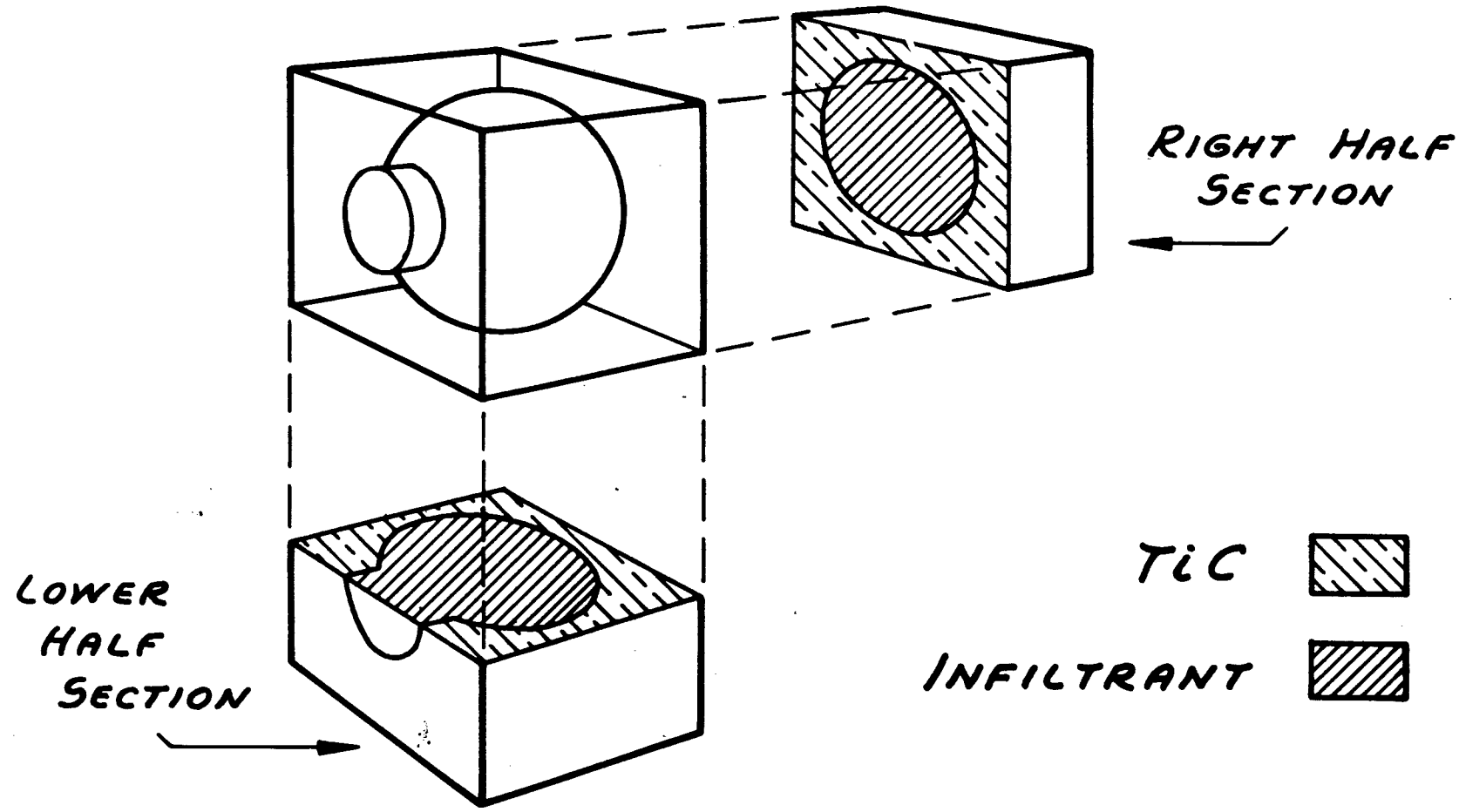


FIG. 16 EROSION OF TiC PARTICLE BY INFILTRANT

The analyses of the four described patterns found in incompletely infiltrated bars (Fig. 14) should be of interest for practical applications. The appearance of one of these patterns gives an indication of the prevailing conditions in the particular run and changes can then be made accordingly.

SECTION IV

INVESTIGATION OF BONDED TITANIUM CARBIDE BARS

A. Introduction

The addition of a metallic binder to titanium carbide serves mainly two purposes: (1) to enhance densification by forming a liquid phase during hot pressing and sintering, and (2) to improve physical properties, such as impact and transverse rupture strength, heat shock resistance and stress-rupture strength at elevated temperatures.

For the evaluation of the different powders and various factors, whose influences were investigated, test bars of 1 in. x 0.40 in. x 0.16 in. were prepared. The final density and transverse rupture strength obtained with these test bars were used as criteria for the evaluation of powders. Densities were measured by water displacement and transverse rupture strengths by cross breaking on a Baldwin Universal Testing Machine over a 9/16 in. span.

B. Sintering in an Atmosphere

Experiments

For the following sintering experiments Kennametal, Metallwerk and Metro-Cutanit powders were used. These materials were ball milled to particle sizes ranging from 1.8 to 3.3 microns in steel or tungsten carbide ball mills. Some of the powders ball milled in a steel mill were leached with hydrochloric acid. Binders used were: (1) 20% Ni, (2) 40% Ni, and (3) 40% Co. Pressing of the mixtures was done:

a) cold at 10 to 15 tsi, after 2% camphor had been added, or
b) hot at 1 to 1-1/2 tsi at temperatures between 1300° and 1500°C in order to avoid loss of binder.

The pieces were sintered in atmospheres of argon or hydrogen at temperatures between 1350° and 1950°C.

Results

No dense pieces were obtained in either one of the experiments. The highest density obtained with 40% binder was about 95% of the theoretical density. All bars produced in this way had a case. In some experiments this case was so small it was hardly visible with the naked eye, while with others the depth was up to 1/4 of the bar.

Discussion

Chemical analyses revealed that binder and free carbon content of the case were much higher and the combined carbon lower than for the rest of the bar. The microstructures of the sintered bars containing 40% nickel or cobalt were very similar to those presented by infiltrated bars (see Fig. 17). TiC particles were rounded and many "C" and "O" shaped forms were present especially with the cobalt-containing bars. The high binder containing case is clearly visible in Fig. 17, a and c.

C. Hot Pressing of Titanium Carbide-Nickel Mixtures to Full Density

Experiments

Kennametal, Metallwerk Plansee and Metro-Cutanit powders, ball milled in a steel mill to 2 - 2.5 microns particle size, were used for experiments designed to investigate the influences of the following factors on the transverse rupture strength of hot pressed nickel-bonded titanium carbide bars:

1. Amount of binder (10 and 20% nickel)
2. Mixing procedure of nickel with TiC
3. Leaching with hydrochloric acid
4. Kind of binder
5. Addition of graphite
6. Production procedure of TiC

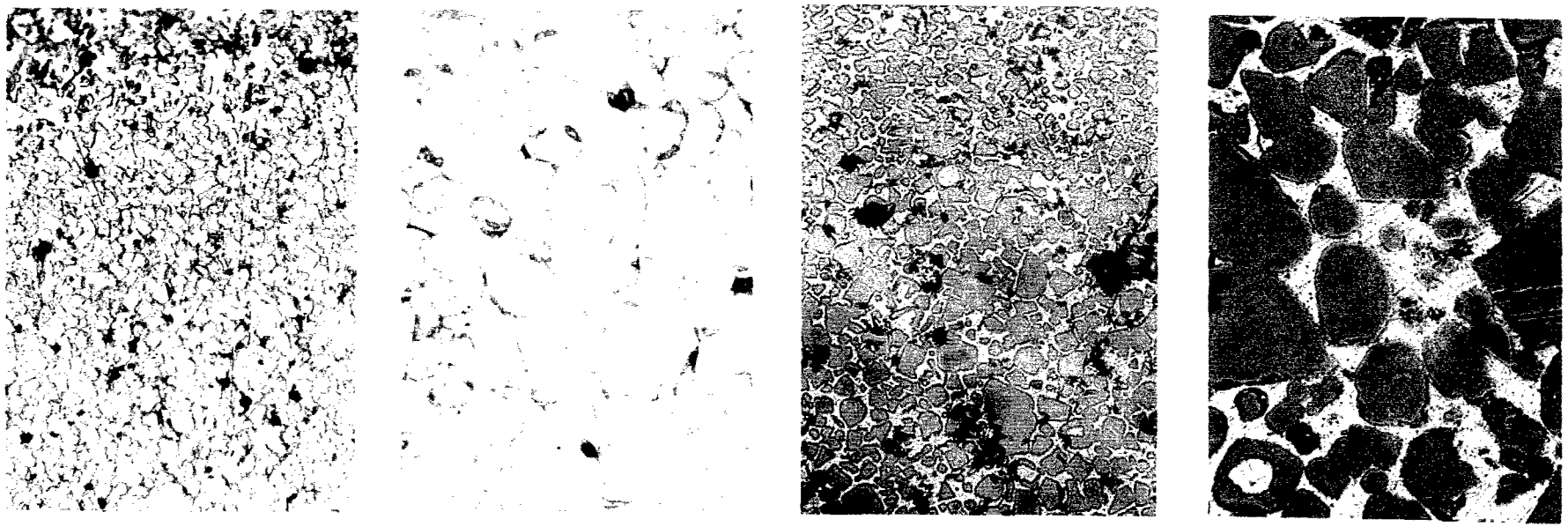
Hot pressing was done at 1 to 1-1/2 tsi at temperatures ranging from 1625° to 1800°C.

Results

Table 17 gives the history of the various powders before mixing with nickel, the mixing procedure, the kind of nickel employed and the maximum transverse rupture strengths obtained. There were at least 8 bars of each powder mixture hot pressed under the same conditions and half of these bars had a better transverse rupture strength than the values given in the last column of Table 17. The results shown in this table can be summarized as follows:

1. An increase in binder content from 10 to 20% increased transverse rupture strength considerably (Experiments 2 and 11) (Figs. 18 and 19).

2. If tumbling was used as the mixing procedure, 1/2 hour tumbling was just as effective as two hours. The transverse rupture strength decreased if tumbling was continued for 20 hours (Experiments 10, 11 and 12). Ball milling was more effective than tumbling for the same length of time (Experi-



X250 a

X1000 b

X250 c

X1000 d

Ball Milled in Steel Mill in H_2O 32 Hours (2.85 microns)

Mixed with 40% Co

Ball Milled in Steel Mill Dry 90 Hours (2.3 microns)

Mixed with 40% Ni

Cold Pressed and Sintered for 1 Hour at 1550°C

Fig. 17 Bonded Titanium Carbide Bars Sintered in Argon (Kennametal)

TABLE 17

TRANSVERSE RUPTURE STRENGTHS OF HOT PRESSED BARS

Exp. No.	Lot No.	Powder Preparation	Mixing Procedure	Kind of Nickel	Transverse Rupture Strength (psi) Maximum	50% Better than
1	K-3		Ball milled with 10% Ni	Electrolytic	98,000	75,000
2	K-3	Leached	10% Ni tumbled 2 hours	Electrolytic	83,000	67,000
3	K-3		10% Ni tumbled 2 hours	Electrolytic	72,000	65,000
4	K-3		20% Ni ball milled 2 hours	Electrolytic	127,000	119,000
5	K-3	+ 5% C	20% Ni ball milled 2 hours	Electrolytic	106,000	98,000
6	K-3	+ 10% C	20% Ni ball milled 2 hours	Electrolytic	70,000	60,000
7	K-3	Leached	20% Ni ball milled 2 hours	Electrolytic	119,000	108,000
8	K-3	Leached	20% Ni ball milled 2 hours	Carbonyl	123,000	116,000
9	K-3	Leached	20% Ni ball milled 2 hours	Annealed Elec.	126,000	109,000
10	K-3	Leached	20% Ni tumbled 1/2 hour	Electrolytic	110,000	98,000
11	K-3	Leached	20% Ni tumbled 2 hours	Electrolytic	109,000	97,000
12	K-3	Leached	20% Ni tumbled 20 hours	Electrolytic	91,000	88,000
13	K-3	Leached	20% Ni tumbled 2 hours	Carbonyl	113,000	103,000
14	K-3	Leached	20% Ni ball milled 20 hours	Carbonyl	132,000	116,000
15	R-3		20% Ni tumbled 2 hours	Electrolytic	129,000	119,000
16	R-4		20% Ni tumbled 2 hours	Electrolytic	131,000	123,000
17	R-1	Leached	20% Ni ball milled 2 hours	Carbonyl	179,000	155,000
18	R-1		20% Ni ball milled 2 hours	Carbonyl	161,000	143,000
19	R-1		20% Ni ball milled 20 hours	Carbonyl	173,000	122,000
20	R-1		20% Ni tumbled 20 hours	Electrolytic	166,000	150,000
21	MC-1		20% Ni tumbled 2 hours	Electrolytic	144,000	134,000

ments 7 and 11, 8 and 13, 19 and 20). A powder ball milled for 20 hours gave a higher transverse rupture strength than one ball milled for two hours (Experiments 14 and 8).

Ball milling to size and mixing with the binder in one operation resulted in higher transverse rupture strength than when mixing with a binder was done in a second operation by tumbling (Experiments 1 and 3).

3. The effect of leaching was not uniform. In two cases leached powders gave higher transverse rupture strengths than unleached ones and in one case this relationship was reversed. When Kennametal powder was tumbled for two hours with 10% electrolytic nickel (Experiments 2 and 3) or when Metallwerk Plansee powder was ball milled for two hours with carbonyl nickel (Experiments 17 and 18), the leached powders gave bars of higher transverse rupture strength than the unleached powders. The reverse relationship was found when Kennametal powder was ball milled for two hours with electrolytic nickel (Experiments 4 and 7). In this case the unleached powder gave bars of higher transverse rupture strength.

4. The influence of the various kinds of nickel was only small (Experiments 7, 8, 9 and 11, 13). Electrolytic nickel annealed in hydrogen was slightly superior to carbonyl nickel and this in turn a little better than as-received electrolytic nickel.

5. An addition of 5 or 10% of graphite together with the binder before ball mill mixing resulted in a gradual decrease in transverse rupture strength (Experiments 4, 5 and 6).

6. Different shipments of powder of the same manufacturer which did not differ in analyses resulted in bars of the same transverse rupture strength (Experiments 15 and 16). The products of different manufacturers, however, although their analyses did not differ to any great extent, produced bars of widely different transverse rupture strengths (Experiments 15, 21 and 11, 19 and 14, 20 and 12). In some of these cases leached and unleached powders were compared with each other, but the differences of transverse rupture strengths obtained were much too great to be traced to the influence of leaching.

Discussion

1. Figs. 18 and 19 show photomicrographs of bars with 10% and 20% nickel, respectively, which had the highest transverse rupture strengths in their respective groups. The pictures show a much better binder distribution and higher density of the 20% nickel containing bar.

2. The first and foremost requirement for mixing TiC with a binder is to obtain a uniform mixture. Several samples of one powder mixture were analyzed chemically for nickel to determine the uniformity of the binder distribution. Highest uniformity was observed after ball milling. Tumbling for two hours also resulted in satisfactory uniformity, while tumbling for 1/2 hour resulted in somewhat less and for 20 hours in much less uniform nickel distribution. The superiority of ball milling over tumbling can be explained by the "smearing" of binder over the entire particle surface during the ball milling operation. This is increased by ball milling for a longer time. Its maximum effect was felt when ball milling to size and mixing was done simultaneously.

3. Leaching of a ball milled powder with hydrochloric acid removed iron picked up from the steel mill as well as TiO_2 formed during ball milling.

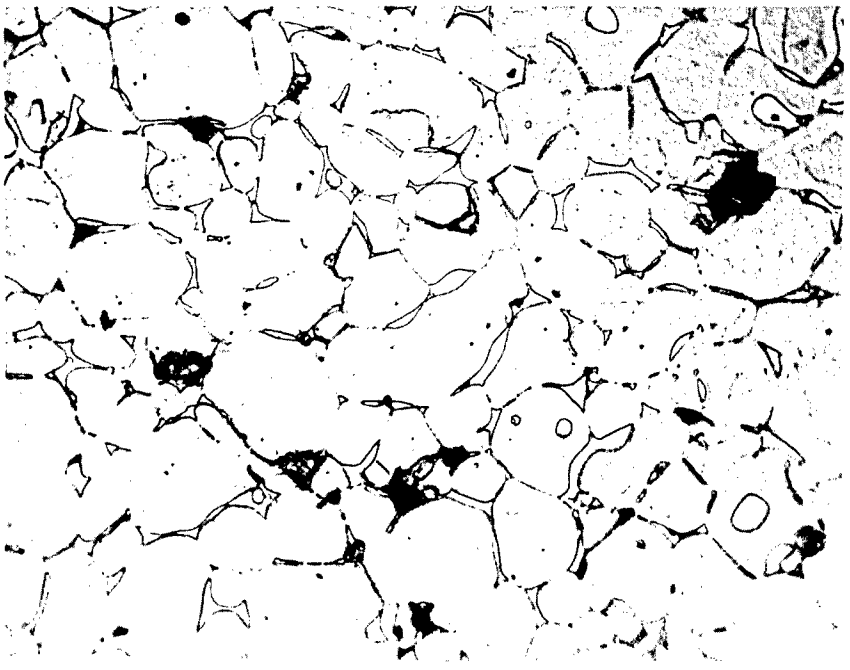


Figure 18. Alk. Sodium Picrate Electrolytic Etch 1000 X
TiC + 10% Ni, Hot Pressed at 1650° C

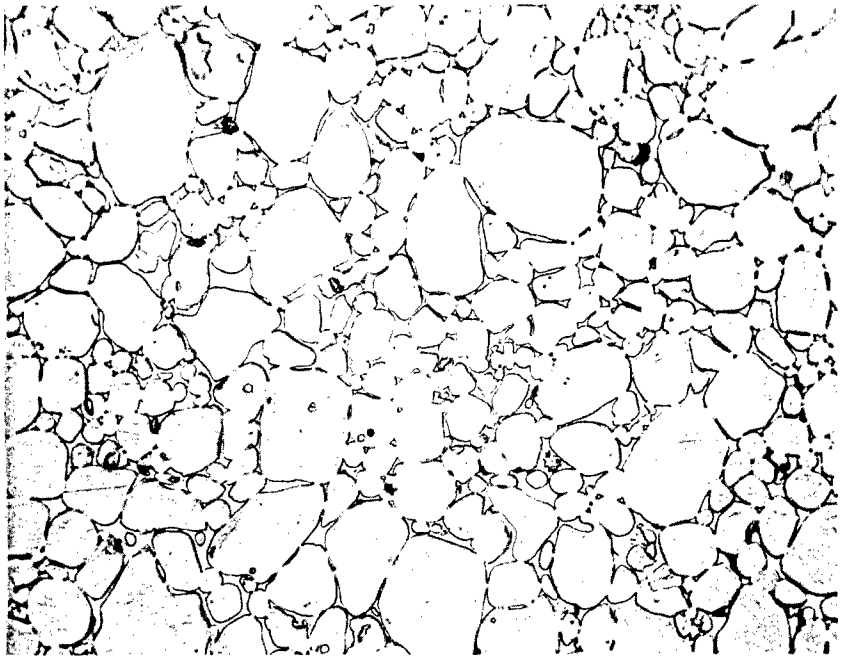


Figure 19. Alk. Sodium Picrate Etch 1000 X
TiC + 20% Ni, Hot Pressed at 1750° C

The specific influences of both these factors will be dealt with later.

4. The influence of the various kinds of nickel was rather a function of its purity than of its origin. The purer the nickel, the higher was the transverse rupture strength. The purity of the electrolytic and carbonyl nickel in the as-received condition was 99.4 and 99.5%, respectively. The annealed electrolytic nickel was 99.7% pure.

5. Five per cent or more of free carbon influenced transverse rupture strength adversely. The influence of the addition of smaller amounts of graphite on hot pressed and vacuum sintered bars will be discussed later.

6. The differences in transverse rupture strengths obtained with the different TiC materials were considerable. They must have their origin in the different production procedures of the investigated powders. These differences were further investigated and will be discussed later with vacuum sintered bars where the same trend was observed.

D. Vacuum Sintering of Titanium Carbide-Nickel Mixtures

1. Introduction

Dense bars with satisfactory transverse rupture strengths could be obtained with the hot pressing procedure described in the foregoing chapter. A wide spread of transverse rupture strengths in one set of bars was frequently encountered. The reason for this was that different amounts of liquid phase were squeezed out during hot pressing. In one lot, for instance, a bar with a transverse rupture strength of 159,000 psi was found to have a Ni content of 18.2%; while another bar of the same material with a transverse rupture strength of 97,000 psi showed only 14.9% Ni. Both bars were 100% dense.

Another difficulty was the determination of the per cent density of a bar. The actual measured density had no meaning as long as the exact binder content was not known. To determine the percent density, the bar had to be destroyed in order to either analyze it chemically or examine it microscopically.

Uniformity of the desired product could not be obtained with the above described hot pressing procedure. It was therefore abandoned and replaced by a combined hot pressing and vacuum sintering procedure which assured constant composition from bar to bar.

2. Vacuum Sintering Procedure for Hot Pressed Bars (Influence of Sintering Time on Transverse Rupture Strength of Various Titanium Carbides)

Experiments

In order to establish proper hot pressing and subsequent vacuum sintering conditions, hot pressing was done at temperatures at which no binder was lost, usually about 1400°C to 1600°C, and bars thus obtained had densities of from 79 to 95% of theoretical density. These bars were then sintered for various lengths of time at temperatures up to 1400°C in a vacuum between 10^{-5} and 10^{-6} mm Hg. Average particle size of the original powders was 2.1 microns.

Results

1. The final density and transverse rupture strength of a bar after vacuum sintering increased with the density of the hot pressed bar (see Fig. 20). For this reason hot pressing should be done at the highest possible temperature. This temperature varied somewhat with the powder, but was always in the vicinity of 1500°C.

2. In order to obtain good densities by vacuum sintering, the hot pressed density should not be below 85% of theoretical density and, if possible, higher.

3. Vacuum sintering for one to two hours at 1350°C resulted in optimum density. An increase in temperature caused loss of nickel; an increase in time caused grain growth which was detrimental to density and transverse rupture strength (see Figs. 21 and 22 and Table 18).

TABLE 18

INFLUENCE OF SINTERING TIME ON TRANSVERSE RUPTURE STRENGTH

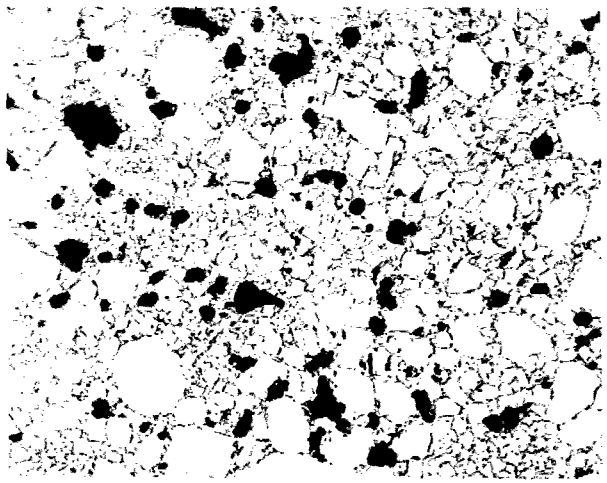
	% Density		Transverse Rupture Strength - psi	
	Kennametal	Metallwerk	Kennametal	Metallwerk
Hot pressed	—	94.8	—	110,000
Vacuum sintered 1 hr.	98	99	126,000	179,000
Vacuum sintered 4 hrs.	98	97	115,000	153,000

4. While these results applied to both investigated materials (Kennametal and Metallwerk), the optimum transverse rupture strengths obtained were a function of the origin of the titanium carbide. In this particular case Metallwerk powder was superior to Kennametal powder.

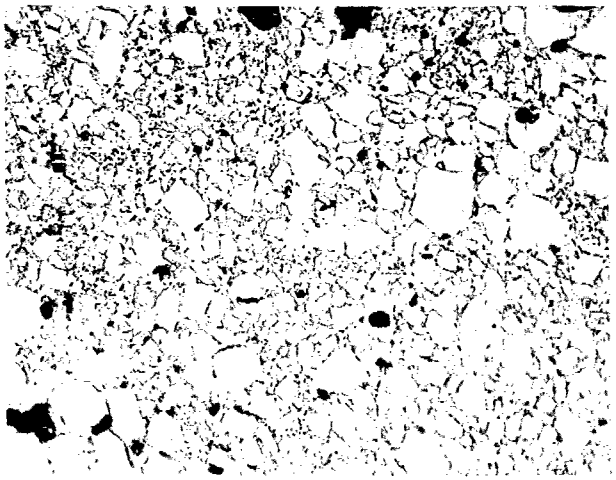
Conclusions

A hot pressing and subsequent vacuum sintering procedure was established which resulted in dense bars. The procedure consisted in hot pressing at the optimum temperature, which for each powder mixture had to be established by a few experimental pressings, and sintering for one to two hours at 1350°C between 10^{-5} and 10^{-6} mm Hg.

The superiority of the Metallwerk powder found its explanation in the fine grained structure of the final bars, while bars produced from Kennametal titanium carbide showed considerable grain growth even after one hour of sintering.



Hot Pressing Temperature - 1300°C
Density after Hot Pressing - 76.1%
Density after Sintering - 94%
Transverse Rupture Strength - 85,300 psi

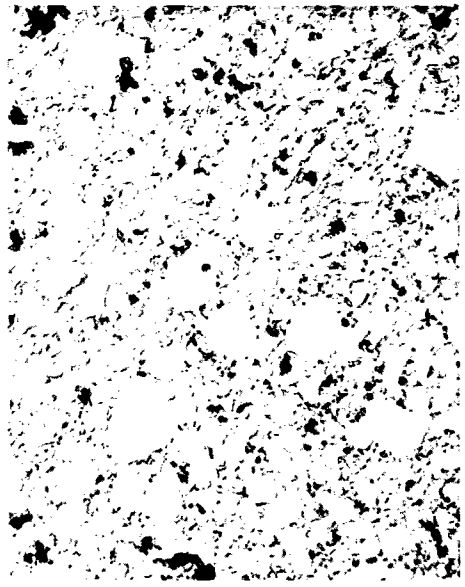


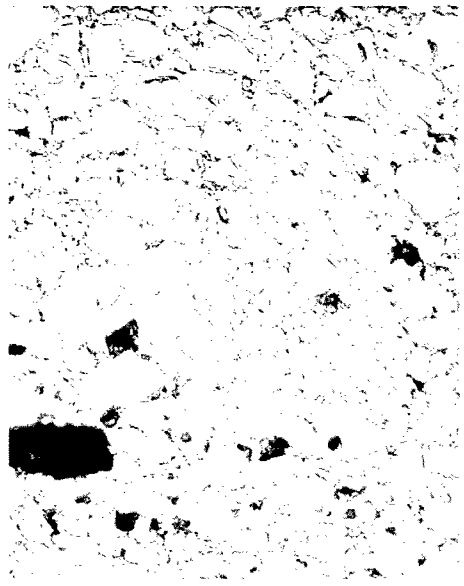
Hot Pressing Temperature - 1560°C
Density after Hot Pressing - 91.2%
Density after Sintering - 97.2%
Transverse Rupture Strength - 122,400 psi

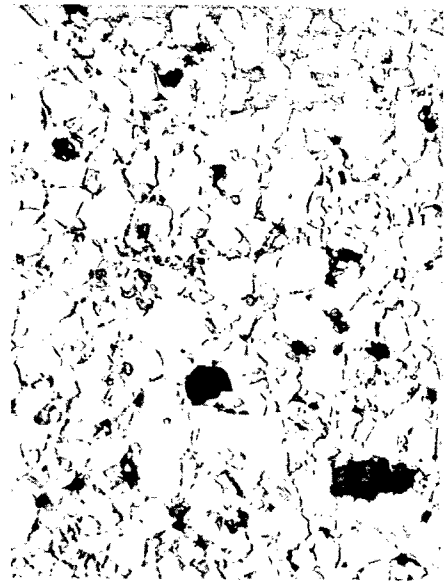
Powder #159; Kennametal, ball milled in steel mill and leached, ball mill mixed with 20% carbonyl Ni for 20 hours.

Magnifications 250X. Alkaline Sodium Picrate Electrolytic Etch

Fig. 20 Bars, Hot Pressed to Different Densities and Vacuum Sintered





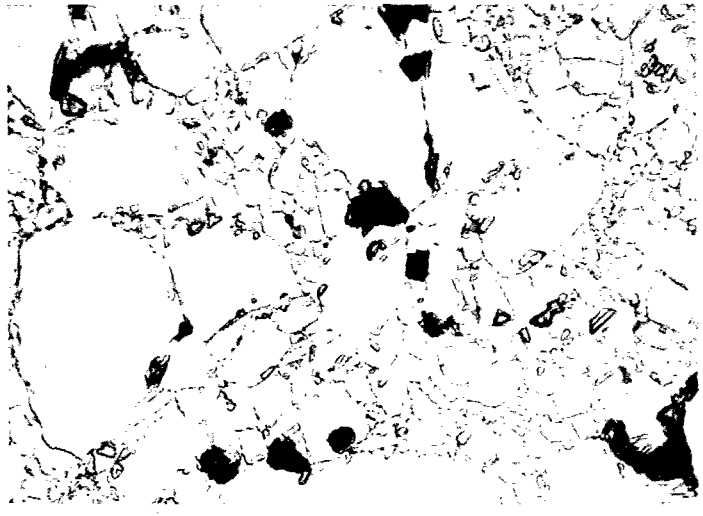


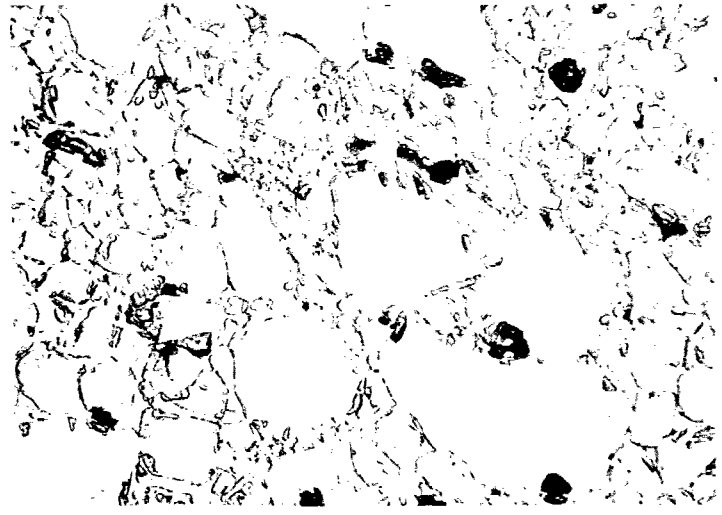
Powder #134; Metallwerk Plansee, Ball Milled 20 Hours in Steel Mill (2.1 microns), Tumbled 20 Hours with 20% Annealed Electrolytic Nickel.

Hot Pressed at - - - 1500° C	Hot Pressed at - - - 1600° C Vacuum Sintered - - 1 hr.	Hot Pressed at - - - 1500° C Vacuum Sintered - - 4 hrs.
Density - - - - - - - 94.8%	Density - - - - - - - 99%	Density - - - - - - - 97%
T.R.S. - - - - - - - - 109,800 psi	T.R.S. - - - - - - - - 178,600 psi	T.R.S. - - - - - - - - 152,500 psi

Magnification 500X. Alkaline Sodium Picrate Electrolytic Etch

Fig. 21 Bars Hot Pressed and Vacuum Sintered





Powder #152; Kennametal, Ball Milled Steel Mill and Leached (2.1 microns), Ball Mill Mixed for 2 Hours with 20% Nickel.

Hot Pressed at - - - - - - - - 1500° C
Vacuum Sintered - - - - - - - - 1 hr.

Density after Hot Pressing - 94.5%
Density after Sintering - - - 98%
Transverse Rupture Strength - 126,000 psi

Hot Pressed at - - - - - - - - 1600° C
Vacuum Sintered - - - - - - - - 4 hrs.

Density after Hot Pressing - 96.5%
Density after Sintering - - - 98%
Transverse Rupture Strength - 115,000 psi

Magnification 500X. Alkaline Sodium Picrate Electrolytic Etch

Fig. 22 Bars Hot Pressed and Vacuum Sintered

3. Vacuum Sintering of Cold Pressed Bars

Introduction

Hot pressing and subsequent vacuum sintering of various Ni-bonded TiC powders resulted in dense bars. It was found, however, that the specific vacuum sintering procedure successfully used for hot pressed bars was not applicable for cold pressed bars. The following study was undertaken in order to establish sintering procedures for cold pressed bars.

Cold Pressing Procedure

In order to avoid pressure cracks, the following cold pressing procedure was found satisfactory. A solution of 3% camphor in ether was added to the TiC-Ni mixture. While the ether was evaporating, the mass was continuously mixed with a spatula until almost dry. Then it was granulated through a 100 mesh screen. The agglomerates formed were of uniform size. Pressing was done immediately, but it was found that the powder in this form could be kept for a week or two in a well sealed jar and still be suitable for pressing. Pressing was done in a double action steel die lubricated with a solution of Sterotex in acetone. Pressure was applied slowly up to 2 tsi. Then the pressure was released and the bar re-pressed with 5 tsi.

Vacuum Sintering Procedure

The vacuum sintering procedure successfully used for hot pressed bars consisted of sintering for 1 to 2 hours at 1350°C in a vacuum of about 5×10^{-5}mm. This treatment did not densify cold pressed bars satisfactorily. It could be expected that either an increase of sintering time or of temperature would improve this condition. However, a higher vacuum pressure would be necessary to prevent loss of binder at the higher temperature.

The following sintering procedures were, therefore, investigated:

1. Increase of sintering time to 3 - 4 hours at 1350°C.
2. Sintering at 1350°C for 1 hour and re-sintering for 1/2 to 1-1/2 hours at 1500°C in a vacuum of 50 microns.
3. Sintering at 1500°C for 5 minutes in a vacuum of 50 microns, decreasing the temperature to 1350°C and holding at this temperature for 1 - 2 hours in a vacuum of 5×10^{-5} mm.
4. Sintering at temperatures from 1500° - 1600°C for 5 to 30 minutes in vacua between 30 and 100 microns.

Results

Kennametal and Metro-Cutanit powders did not densify satisfactorily with any of these procedures, while Metallwerk Plansee powder densified using any one of these procedures. The transverse rupture strengths obtained were practically identical for all sintering procedures but were inferior to the ones reached with hot pressed bars. Table 19 compares the densities and maximum transverse rupture strengths of hot pressed and vacuum sintered bars with those obtained by cold pressing and vacuum sintering. The range given for the transverse rupture strengths of cold pressed bars shows the small variations encountered using the above sintering procedures.

TABLE 19

DENSITIES AND TRANSVERSE RUPTURE STRENGTHS OBTAINED AFTER VACUUM SINTERING OF HOT PRESSED AND COLD PRESSED BARS

(Metallwerk Plansee Powder)

Powder No.	Ball Milling Procedure*	Particle Size (Microns)	Max. Density (%) H.P.	Max. Density (%) C.P.	Max. TRS (kpsi) H.P.	Max. TRS (kpsi) C.P.
193	Simultaneously milled & mixed, WC mill, 72 hrs	2.2	98	97	198	108
199	Milled WC mill, 72 hrs, mixed 20 hrs	2.0	100	98	176	121
200	Milled steel mill, WC balls, 72 hrs, mixed 20 hrs	1.8	99	97-99	146	120-130
201	Milled WC mill, 168 hrs, mixed 20 hrs	1.5	100	97-99	170	122-128
205	Simultaneously milled & mixed, WC mill, 192 hrs	1.8	99	98-100	170	131-140

* All powders mixed with 20% nickel.

Conclusions

Bars cold pressed from Metallwerk Plansee powder could be vacuum sintered to full density by sintering either for 4 hours at 1350°C or 15 minutes at 1600°C. However, the transverse rupture strengths of bars sintered in either way were below those obtained with hot pressed and vacuum sintered bars.

More satisfactory results with cold pressed bars were obtained when ball milling was done for 144 hours with carbon tetrachloride. These experiments are found in chapter D.-14 on "Influence of Pressing Procedure".

4. Influence of Particle Size

Experiments

1. In the section on "Flotation", it was pointed out that flotation fractions of Kennametal powder varied notonly in graphite content, but also in particle size. These fractions were ball mill mixed with 20% carbonyl nickel in a steel mill for 2 hours.

2a. Mixtures of Kennametal powder and 20% carbonyl nickel were ball milled dry for 72 and 96 hours, respectively, in a tungsten carbide mill. The ball to load ratio was 6:1.

2b. The same mixtures as under 2a were ball milled in acetone in a tungsten carbide mill using a ball to load ratio of 6:1 and 12:1, respectively.

All powder mixtures were hot pressed and vacuum sintered.

Results

1. The results obtained with the various flotation fractions are given in Table 20 and plotted in Fig. 23. Smaller particle size of the starting material resulted in higher transverse rupture strength. Fig. 24 shows photomicrographs of two bars of Table 20 with 131,000 and 93,000 psi transverse rupture strengths, respectively. The large differences in grain sizes are obvious.

TABLE 20

INFLUENCE OF PARTICLE SIZE ON DENSITY AND TRANSVERSE RUPTURE STRENGTH

(Kennametal Powder, Floated and Ball Mill Mixed with 20% Ni in Steel Mill)

Powder No.	Particle Size Microns	Graphite %	Density g/cc	Density %	TRS (kpsi) Maximum	TRS (kpsi) 50% Better Than
182	1.6	0.32	5.30	98	131	121
184	1.9	0.06	5.37	99	123	118
185	2.4	0.02	5.21	96	105	103
183	3.5	0.06	5.14	95	93	84

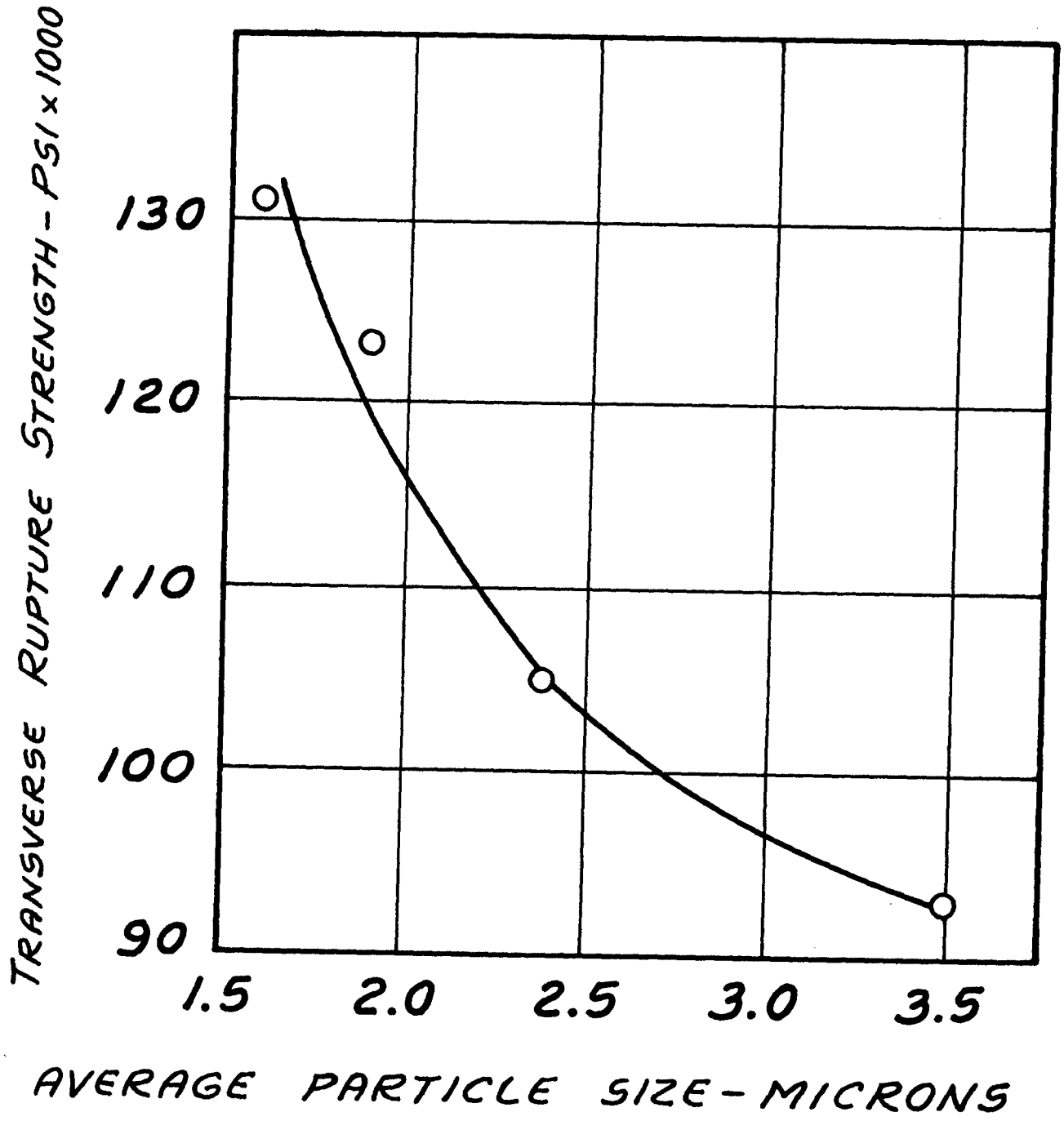
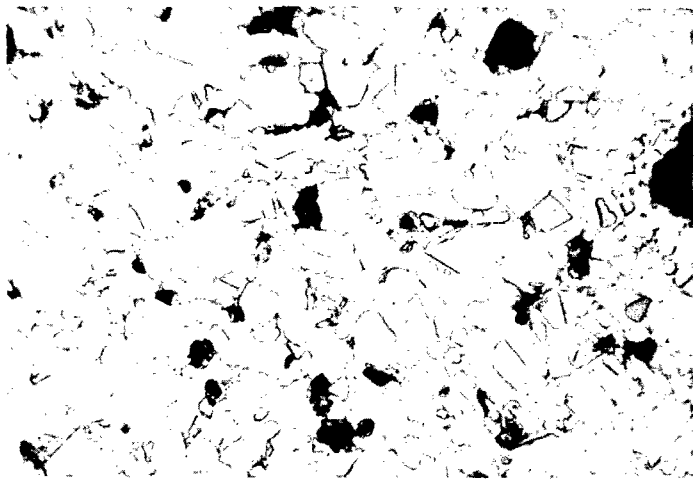
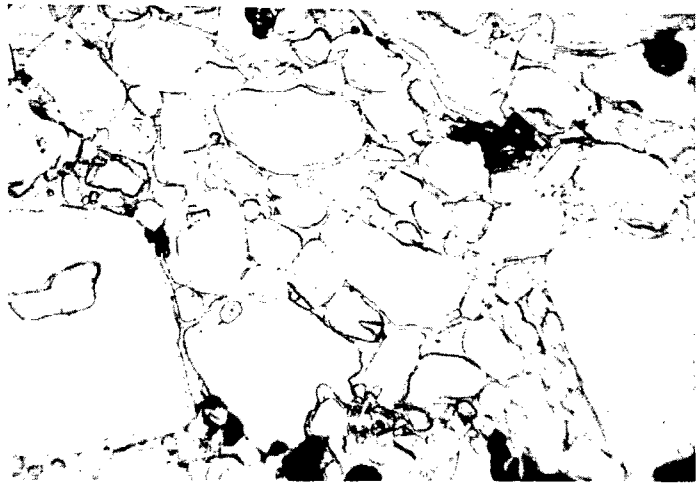


FIG. 23 RELATIONSHIP BETWEEN PARTICLE SIZE AND TRANSVERSE RUPTURE STRENGTH.





Kennametal, Ball Milled in Steel Mill for 42 Hours and Floated

Powder #182; Overflow (1.6 microns) ball mill mixed with 20% carbonyl Ni for two hours.

Powder #183; Tailings (3.5 microns) ball mill mixed with 20% carbonyl Ni for two hours.

Hot Pressed at 1500° C, Vacuum Sintered 1 Hour at 1350° C

Density 98% - T.R.S. 130,800 psi

Density 95% - T.R.S. 93,000 psi

Magnification 1000X. Alkaline Sodium Picrate Electrolytic Etch

Fig. 24 Bars Produced Under Identical Conditions from Particle Size Fractions of Same Powder

2. The results obtained with the powders ball milled either dry or wet in the tungsten carbide mill were tabulated in Table 21. The amounts of graphite in these powders were between 0.1 and 0.15%, the amount of oxygen 0.5%. The table shows:

(a) Ball milling in the presence of a liquid resulted in a smaller particle size (compare powders 230 and 217). This effect could not be generalized; it was due to the fact that the liquid prevented caking of the powder which always happened in this particular mill when dry ball milling was done.

(b) The change to a higher ball to load ratio resulted in a smaller particle size for the same ball milling time.

TABLE 21

INFLUENCE OF PARTICLE SIZE ON DENSITY AND TRANSVERSE RUPTURE STRENGTH

(Kennametal Powder Ball Milled to Size and Mixed Simultaneously with 20% Ni in WC Mill)

Powder No.	Ball Milling Treatment	Ball/Load Ratio	Particle Size Microns	% WC	Density g/cc	Density %	TRS (kpsi) Max.	TRS (kpsi) 50% Better Than
230	72 hrs. dry	6:1	2.7	1.80	5.25	96	113	108
239	96 hrs. dry	6:1	2.1	1.92	5.36	98	133	129
217	72 hrs. acetone	6:1	2.2	4.76	5.39	96	135	119
238	72 hrs. acetone	12:1	1.2	4.71	5.58	100	159	154

Conclusions

Densities and transverse rupture strengths of hot pressed and vacuum sintered bars were a function of the particle size of the titanium carbide powder. The beneficial influence of smaller particle size was especially obvious from the high density and transverse rupture strength obtained with powder 238 (Table 21).

5. Influence of Free Carbon

Experiments

Four of the investigated powders were ball milled to size in a tungsten carbide mill and mixed simultaneously with 20% nickel and graphite, the amount of which varied from 0.5 to 2%. The mixtures were hot pressed and vacuum sintered for 2 hours at 1350°C.

Results

Evaluation of the results of Table 20, with respect to the amounts of free carbon present in the different flotation fractions, indicated that small amounts of graphite had no effect on transverse rupture strength of

Kennametal bars or that any effect was overshadowed by the influence of the particle size.

Table 22 compares densities and transverse rupture strengths of vacuum sintered bars produced from the original powders with those obtained with powders to which additions of graphite had been made.

TABLE 22

INFLUENCE OF FREE CARBON ON TRANSVERSE RUPTURE STRENGTH

Powder No.	Lot No.	Particle Size (Microns)	C %	Density %	TRS (kpsi) Maximum	TRS (kpsi) 50% Better Than
234	K-4*	1.9	0.09	100	152	148
239	K-4	2.1	0.46	98	133	129
219	K-4	2.2	0.99	94/97	133	129
220	K-4	2.3	2.02	84/87	not determined	
242	R-1*	2.3	0.56	99	210	204
243	R-1	2.2	1.20	99	192	188
244	R-1	2.1	1.72	99	188	181
211	MC-1*	2.4	0.40	99	166	154
264	MC-1	2.1	1.86	99	170	145
232	T-3*	2.3	0.19	97	155	153
262	T-3	2.1	0.50	99	149	137
263	T-3	2.1	1.48	99	150	145

* The letters indicate the manufacturer:
K: Kennametal Inc.
R: Metallwerk Plansee
MC: Metro-Cutanit, Ltd.
T: Titanium Alloy Mfg. Co.

Density and transverse rupture strength of Kennametal powder dropped, the latter from 152,000 psi to 133,000 psi when 1/2% of graphite was added (Table 22). With 1% of graphite a density of only 94% could be reached in the normal vacuum sintering operation. A second vacuum sintering brought the density up to 97% and the transverse rupture strength to 133,000 psi. When 2% of graphite wasadded, the first sintering resulted in a density of 84% and the second sintering in 87%.

Metallwerk Plansee powder as received contained about 1/2% of graphite. This was brought up by additions to 1.2 to 1.7%, respectively, without impairing the final densification. The transverse rupture strength dropped only slightly (10%).

An additional 1.5% of graphite to Metro-Cutanit powder did not affect densification or transverse rupture strength in any way.

Titanium Alloy's original graphite content of 0.2% could be raised to 0.5 and 1.5% without any effect on density or transverse rupture strength.

Conclusions

The effect of the presence of free carbon on densification and transverse rupture strength varied with the different powders. Up to a certain limit, which might differ with the origin of the powder, free carbon did not affect densification and transverse rupture strength to a high degree. It is, of course, possible that titanium carbide containing very little or no free carbon may produce compacts of superior physical properties. The production difficulties of such a material might, however, make it commercially unfeasible.

6. Influence of Ball Mill Material (Influence of Iron and Tungsten Carbide)

Experiments

Experiments were designed in such a way that various amounts of iron or tungsten carbide and combinations of these two were picked up in ball milling. Kennametal powder was ball milled to size,

(a) in a steel mill with steel balls for various lengths of time,
(b) in a steel mill with WC balls,
(c) in a WC mill with WC balls,
(d) in a steel mill with the addition of 3% WC.

Mixing with 20% carbonyl nickel was done either in a steel mill or in a tungsten carbide mill for 24 hours.

Results

Iron and tungsten analyses of the powders, particle sizes and transverse rupture strengths are given in Table 23, from which the following conclusions can be drawn:

1. The influence of iron on the transverse rupture strength was small (see Powders 212 and 159); in the presence of WC it was negligible (see Powders 178, 210 and 195). The relatively small amounts of iron, compared to the 20% nickel addition, are believed to be dissolved in the binder phase.

2. The strong influence of WC was obvious from a comparison of the transverse rupture strengths of Powders 212 and 210 which differ only in the presence of about 3% WC.

3. It was irrelevant whether the WC content of a powder was acquired by ball milling in a WC mill or by addition of WC to the powder before ball milling in a steel mill. A WC mill was used in size reduction and mixing of Powder 195, while a steel mill was used in both operations for Powder 210, where the 3% WC was added before ball milling.

4. According to the photomicrographs of some of these bars, shown in Section V, the bars have a high density (Fig. 26a shows Powder 212; Fig. 27a, Powder 195; and Fig. 30, Powder 210). The theoretical density could not be calculated with accuracy because of the formation of solid solutions.

TABLE 23

INFLUENCE OF Fe AND WC ON TRANSVERSE RUPTURE STRENGTH

(Kennametal Powder)

Powder No.	Ball Mill	Particle Size Microns	Analysis % Fe	Analysis % W	TRS (kpsi) Maximum	TRS (kpsi) 50% Better Than
212	Steel	2.1	1.63	-	111	109
159	Steel	1.9	0.21	-	122	115
196	Steel, WC Balls	1.5	0.89	2.1	140	129
178	WC	1.6	0.17	2.3	149	138
210	Steel*)	2.1	1.48	2.6	148	140
195	WC	1.9	0.38	3.8	152	137

*) WC added

7. Influence of Molybdenum Carbide

Experiments

The beneficial influence of the presence of tungsten carbide on the transverse rupture strength of hot pressed and vacuum sintered bars has been discussed in the previous chapter.

In the present investigation, the following experiments were made:

1. 1.5% Mo_2C together with 20% Ni was ball mill mixed in a steel mill with Kennametal powder, which had been ball milled to size in the same mill.
2. Metallwerk Plansee powder was ball milled to size in a steel mill and half of the thus obtained powder leached with hydrochloric acid. Both fractions were ball mill mixed with 1.5% Mo_2C and 20% Ni for 24 hours.

Results

The results are given in Tables 24 and 25. In Table 24 maximum densities and transverse rupture strengths obtained with Kennametal powder without additions and with additions of Mo_2C and WC are compared. Table 25 shows transverse rupture strengths obtained with leached and unleached Metallwerk Plansee powder to which Mo_2C had been added. The densities obtained with Metallwerk powders were about 100%.

TABLE 24

INFLUENCE OF Mo_2C AND WC ON TRANSVERSE RUPTURE STRENGTH

(Kennametal Powder)

Powder No.	Particle Size Microns	Addition	Density %	TRS (kpsi) Maximum	TRS (kpsi) 50% Better Than
159	1.9	None	97	122	115
212	2.1	None	98	111	109
226	2.2	1.5% Mo_2C	100	119	115
210	2.1	3% WC	100	148	140

TABLE 25

INFLUENCE OF Mo_2C ON TRANSVERSE RUPTURE STRENGTH

(Metallwerk Plansee Powder)
(All bars were vacuum sintered for 2 hours)

Powder No.	Particle Size Microns	Leached	Addition	TRS (kpsi) Maximum	TRS (kpsi) 50% Better Than
134/N20	2.1	No	None	179	166
236	2.0	No	1.5%	148	130
237	2.0	Yes	1.5%	159	147

Conclusions

1. The addition of Mo_2C or WC to Kennametal powder enhanced densification. The reason why complete densification was obtained with Metallwerk Plansee powders without these additions was that these powders already contained some molybdenum and tungsten, very probably in the form of carbides, as impurities.

2. While the presence of WC raised transverse rupture strength of hot pressed and vacuum sintered bars considerably, besides helping densification, Mo_2C had no such effect; on the contrary, it might even have lowered the transverse rupture strengths somewhat (see Table 25). The fact that Powder 226 produced bars of higher transverse rupture strengths than 212 (Table 24) is believed to be the effect of higher density, rather than of Mo_2C. Both Powders 159 and 212 (Table 24) had about the same transverse rupture strengths without Mo_2C addition as Powder 226, although the densities

of the bars were lower.

8. Influence of Chromium Carbide and Tantalum Carbide

The influence of the presence of tungsten carbide (WC) and molybdenum carbide (Mo_2C) on the transverse rupture strength of hot pressed and vacuum sintered bars has been discussed in previous chapters.

Experiments

In the present investigation Kennametal powder was ball milled in a steel mill to 2.3 microns average particle size. One-third of the fine powder was used in the as-ball milled condition, another third was leached with hydrochloric acid and the final third with acetic acid. Each of the three fractions was subdivided into two parts and mixed with 20% nickel and either 3% Cr_3C_2 or 3% TaC by ball milling. The mixtures were hot pressed and vacuum sintered.

Results

1. All three mixtures with Cr_3C_2 hot pressed normally to densities of about 95%. Vacuum sintering, however, did not result in any further densification; and maximum transverse rupture strengths were about 70,000 psi. When the first of the three mixtures was ball milled for an additional 24 hours in order to obtain a somewhat smaller particle size and better mixing, the improvement obtained in densification and transverse rupture strength was negligible.

2. Table 26 compares densities and transverse rupture strengths of the TaC containing mixtures with properties obtained with specimens not containing this addition.

TABLE 26

INFLUENCE OF TaC ON TRANSVERSE RUPTURE STRENGTH

(Kennametal Powder)

Powder No.	Particle Size Microns	Leach	Addition	Density %	TRS (kpsi) Maximum	TRS (kpsi) 50% better than
159	1.9	HCl	None	97	122	115
212	2.1	None	None	98	111	109
257	2.0	HAc	3% TaC	97	116	108
258	1.9	HCl	3% TaC	98	125	116
259	1.9	None	3% TaC	98	117	98

Conclusions

1. Addition of 3% Cr_3C_2 to TiC prevented densification during vacuum sintering under the investigated conditions. The microstructure showed considerable grain growth, coring of practically every particle and a non-uniform binder distribution. With all three mixtures the oxygen content of the specimens increased during vacuum sintering, which is usually not the case. A typical specimen had 0.33% oxygen as powder and 0.47% as vacuum sintered.

2. The addition of 3% TaC to TiC had no marked effect on densification or transverse rupture strength.

9. Influence of Oxygen

Experiments

To investigate the influence of the presence of oxygen on physical properties, TiO and TiO_2, respectively, were added to Kennametal TiC and ball mill mixed with 20% nickel. Hot pressing of these mixtures encountered difficulties. The oxides obviously reacted with the graphite die causing sticking and cracking of the bars.

Accidentally a tungsten carbide mill sprang a leak and lost half of its load changing the ball to load ratio from 6:1 to 12:1. This increased the rate of particle size reduction and resulted in a higher oxygen pickup than normal, probably in the form of an oxide film. The powder thus produced was compared with a powder produced in a normal ball milling procedure.

Results

Powder 208 produced in the leaking ball mill picked up almost twice as much oxygen as powder 234, although it was ball milled for a shorter time (72 hours instead of 96). The particle size of powder 208 was a little smaller and the WC pickup a little higher due to the changed ball to load ratio caused by the loss of powder. Table 27 gives partial analyses for each of the two powders and for the original material, as well as densities and transverse rupture strengths of hot pressed and vacuum sintered bars. The data show slight differences in transverse rupture strengths probably due to differences in particle sizes.

Conclusions

1. In the investigated range (0.4 - 0.9% O_2), the amount of oxygen picked up during ball milling did not influence densification during hot pressing and vacuum sintering, and the transverse rupture strengths obtained were only a function of the particle size under otherwise identical conditions.

2. The reproducibility of density and transverse rupture strength by hot pressing and vacuum sintering of bars produced from the same powder after separate ball milling was satisfactory.

TABLE 27

INFLUENCE OF OXYGEN ON DENSIFICATION AND STRENGTH

(Kennametal Powder)

Powder No.	C (Graphitic)	Particle Size Microns	Analysis % O_2	Ni	W	Density g/cc	TRS (kpsi) Max.	50% Better Than
Original	0.17	23	0.14	--	--	--	--	--
208	0.17	1.7	0.86	19.05	2.92	5.52	161	151
234	0.13	1.9	0.47	19.75	2.17	5.49	152	148

10. Influence of Leaching

Ball milling of titanium carbide powder in a steel mill resulted in an increase in the iron and oxygen content, which was a function of ball milling time (Section I, Tables 4 and 5). Leaching such a powder with hydrochloric acid removed most of the picked up iron and oxygen (Section I, Table 8).

Table 28 compares densification and transverse rupture strengths obtained with unleached and hydrochloric acid leached Metallwerk and Kennametal powders and shows a slight but clear superiority of the leached materials. The same trend was shown by the figures of Tables 25 and 26. On the other hand, Table 26 showed that an acetic acid leach, which removed iron, did not affect transverse rupture strength, and from Table 27 it could be learned that small differences in the oxygen content did not influence transverse rupture strength either. From these contradictory results the conclusion must be drawn that small amounts of iron or oxygen do not affect transverse rupture strength appreciably.

TABLE 28

INFLUENCE OF LEACHING

Powder No.	Lot No.	Particle Size Microns	Leached	Density g/cc	TRS (kpsi) Max.	50% Better Than
134/N20	R-1	2.1	No	5.36	153	140
163	R-1	2.1	Yes	5.40	170	157
212	K-4	2.1	No	5.31	111	109
152	K-3	2.1	Yes	5.32	125	117

11. Influence of the Kind of Nickel Used as Binder

It was reported in the chapter on "Hot Pressing of TiC-Ni Mixtures to Full Density" that with various kinds of Ni (electrolytic, annealed electrolytic and carbonyl Ni) used as binder, transverse rupture strength increased with the purity of the nickel. Annealed electrolytic nickel was found to be purer than carbonyl nickel, and this in turn purer than non-annealed electrolytic Ni. The same relationship was found to be true in the case of hot pressed and vacuum sintered pieces. For instance, bars of Kennametal TiC produced under identical conditions had a maximum transverse rupture strength of 122,000 psi when carbonyl Ni was used as binder, and 126,000 psi when annealed electrolytic Ni was used. Although these differences were real, they were so small that it was considered more expedient to use as-received carbonyl Ni for most of our experiments in order to eliminate the annealing process.

12. Influence of Ball Milling Procedure and Ball Milling Time on Transverse Rupture Strength

Materials received from Metallwerk Plansee, Metro-Cutanit, Kennametal, Titanium Alloy and Norton Company were used for these experiments, the latter one after a flotation purification.

Ball Milling Procedures

A tungsten carbide ball mill was used exclusively for all the following millings:

1. The powders under investigation were ball milled for 72 hours, which reduced the average particle size to about 2 microns. Twenty per cent carbonyl nickel was then added and ball milling continued for another 24 hours.
2. The powders, plus 20% carbonyl nickel, were introduced together into the ball mill and size reduction and mixing performed simultaneously for 72 hours, reducing the particle size to about 2.2 microns. The powder supplied by Titanium Alloy had to be ball milled for 96 hours in order to obtain the same particle size reduction.
3. Metallwerk Plansee powder was ball milled for 168 hours, which reduced its particle size to 1.3 microns. Twenty per cent carbonyl nickel was then added and ball milling continued for 20 hours.
4. Metallwerk Plansee powder, together with 20% carbonyl nickel, was ball milled for 192 hours. The average particle size of the mixture was 1.8 microns.
5. Titanium Alloy powder, together with 20% carbonyl nickel, was ball milled 144 hours. The average particle size of the mixture was 1.8 microns.

All powders were hot pressed and vacuum sintered according to previously described procedures.

Results

Bars produced from Norton powder did not densify properly and the

transverse rupture strength obtained should, therefore, not be compared with that of dense bars. Good densities were obtained with all the other materials. The results are shown in Tables 29 and 30.

Table 29 compares the transverse rupture strengths of dense bars (with the exception of Norton powder) obtained with various powders using two ball milling procedures:

1. Ball milling to size and mixing in two steps according to method 1, and
2. Ball milling to size and mixing in one step according to method 2.

With both these procedures, Metallwerk Plansee powder showed a slight but clear superiority. Not only was the maximum transverse rupture strength of Metallwerk bars higher than the other two, but 50% of the Metallwerk bars showed a higher transverse rupture strength than the maximum transverse rupture strength of bars produced from the other powders.

As far as the procedures are concerned, the second -- ball milling to size and mixing simultaneously -- was superior to the two-step procedure. Here, again, differences were slight but distinct; for 50% of the bars produced by the one-step procedure, the transverse rupture strength was higher than the maximum transverse rupture strength of bars produced by the two-step procedure.

Table 30 compares the same two procedures, using Metallwerk Plansee powder, with two similar procedures in which only the ball milling time was varied. A comparison of the results of procedures 1 and 2 with 3 and 4 shows that increased ball milling time resulted in lower transverse rupture strengths. The one-step procedure (4) proved to be superior to the two-step procedure (3), considering that 50% of the bars made by this procedure had a transverse rupture strength better than 169,000 psi, while the comparative figure for procedure 3 was only 141,000 psi.

Titanium Alloy powder, ball milled for 144 hours, produced bars with a maximum transverse rupture strength of 157,000 psi (50% better than 152,000 psi), which is hardly an improvement over the figures given for the same material in Table 29.

Conclusions

With these experiments, a production procedure for making dense bars from various powders had been established. This procedure consisted of ball milling to size and mixing with the binder simultaneously for 72 hours in a tungsten carbide mill, hot pressing at 1500°C and then vacuum sintering at 1350°C for 1 hour. An increase of ball milling time resulted in lower transverse rupture strength for Metallwerk Plansee and no further improvement for Titanium Alloy powder. It is believed that the conclusion can be drawn that a similar result would be obtained with the other powders.

TABLE 29

TRANSVERSE RUPTURE STRENGTHS (PSI) OBTAINED WITH VARIOUS POWDERS

Supplier	Lot #	Procedure 1*		Procedure 2*	
		Maximum	50% Better Than	Maximum	50% Better Than
Metallwerk Plansee	R-1	176,000	169,000	198,000	194,000
Metro-Cutanit	MC-1	152,000	147,000	166,000	154,000
Kennametal	K-4	152,000	137,000	161,000	155,000
Titanium Alloy	T-3	--	--	155,000	153,000
Norton	N-3	73,000	67,000	--	--

TABLE 30

TRANSVERSE RUPTURE STRENGTHS (PSI) OBTAINED

WITH METALLWERK PLANSEE POWDER

Procedure*	Maximum	50% Better Than
1	176,000	169,000
2	198,000	194,000
3	170,000	141,000
4	170,000	169,000

* The procedure numbers refer to the respective paragraphs under Ball Milling Procedures.

13. Influence of Ball Milling Medium on Transverse Rupture Strength

Experiments

For this investigation, carbon tetrachloride, hexane, ethyl alcohol, and acetone were used as ball milling liquids. Kennametal TiC plus 20% carbonyl nickel was introduced into the WC mill which was then filled almost completely with the respective liquid. Ball milling time was 72 hours. The content of the ball mill was filtered and the powder vacuum dried. Powders were then hot pressed and vacuum sintered as described above.

Results

Table 31 shows maximum densities and transverse rupture strengths obtained as well as other pertinent data. Powder 208 was added for comparison.

TABLE 31

INFLUENCE OF THE BALL MILLING MEDIUM ON TRANSVERSE RUPTURE STRENGTH

(Kennametal Powder)

Powder No.	Ball Milling Medium	Particle Size Microns	Oxygen %	WC %	Maximum Density g/cc	Maximum Density %	TRS (kpsi) Max.	TRS (kpsi) 50% Better Than
208	Air	1.7	0.86	3.10	5.52	100	161	155
215	Hexane	1.7	0.47	5.14	5.57	100	144	131
216	Ethyl Alcohol	2.3	0.31	3.92	5.72	100	155	143
217	Acetone	2.2	0.50	4.76	5.39	96	135	119
214	Carbon Tetra-chloride	2.3	0.53	3.82	5.10	93	90	89

The oxygen pickup was less when ball milling was done in a liquid. But this was the case only when the ball mill was almost filled up completely with the liquid. The original powder had an oxygen content of 0.14%.

The powders ball milled with acetone and carbon tetrachloride did not come up to full densities. The differences in measured densities for 100% dense bars were due to variations in WC pickup and binder content.

Conclusions

As pointed out in a previous chapter the use of a liquid ball milling medium prevented caking of the powder in the ball mill and, therefore, shortened the ball milling time necessary to reach a certain particle size. Besides this advantage, the foregoing experiments did not reveal any beneficial influence of wet ball milling over dry ball milling.

The oxygen pickup was lower due to the exclusion of air and the WC pickup was higher.

14. Influence of Pressing Procedure on Different Powders Ball Milled in Carbon Tetrachloride

Experiments

Five titanium carbide powders supplied by Kennametal, Metallwerk Plansee, Metro-Cutanit, Titanium Alloy and Norton Company were ball milled to about one micron average particle size and mixed simultaneously with 20% nickel in a tungsten carbide mill with carbon tetrachloride as ball milling medium for 144 hours. The fine powders were compacted by the following three different pressing procedures:

a) dried and hot pressed
b) dried and cold pressed
c) cold pressed in the wet condition (wet pressed).

Norton titanium carbide, received in lumps, was crushed to -100 mesh and subjected to a flotation process in order to bring its graphite content in line with that of the other three powders, which were ball milled in the as-received condition.

The bars were vacuum sintered as usual for 2 hours at 1350°C in a vacuum of between 10^{-5} and 10^{-6} mm Hg.

Results

Results were tabulated in Table 32. Most wet pressed bars cracked during sintering. No results were, therefore, reported on this procedure. Good densification was obtained with both, hot pressing and cold pressing, techniques. Only Titanium Alloy powder did not densify satisfactorily when cold pressed. For Kennametal and Metallwerk powders hot pressing resulted in higher transverse rupture strength than cold pressing, while for Metro-Cutanit and Norton powders both techniques were equal. The micro-structures of all vacuum sintered bars were very similar to the one of Kennametal material shown in Section V, Fig. 33c.

Conclusions

Ball milling in a tungsten carbide mill with carbon tetrachloride as ball milling medium for 144 hours resulted in powders of about one micron average particle size. Hot or cold pressing and vacuum sintering of these powders after vacuum drying resulted in good densification. The variations in transverse rupture strengths of the different materials must be considered characteristic for the particular powders. The relatively low transverse rupture strength of Norton powder has probably its reason in its high oxygen content, part of which is believed to be in the form of TiO in solid solution with TiC.

TABLE 32

INFLUENCE OF PRESSING PROCEDURE

Powder No.	Lot No.	O_2 %	Pressing Procedure	Density g/cc	Density %	TRS (kpsi) Maximum	TRS (kpsi) 50% Better Than
171	K-4	1.71	hot	5.48	99	161	135
			cold	5.48	99	139	123
246	R-1	1.02	hot	5.33	98	174	163
			cold	5.36	98	157	154
260	MC-1	0.84	hot	5.21	97	151	146
			cold	5.28	98	154	146
253	N-3	3.13	hot	5.42	99	112	83
			cold	5.38	97	116	105
254	T-3	0.62	hot	5.44	100	204	177
			cold	5.10	94	not determined	

E. Summary

For the production of bonded titanium carbide bars, the following three procedures were investigated:

1. The TiC-binder mixtures were cold pressed and sintered under a protective atmosphere.
2. The mixtures were hot pressed at various temperatures,
3. The mixtures were either hot pressed at a relatively low temperature or cold pressed, and then vacuum sintered.

The first procedure resulted in non-uniform pieces, containing a binder rich surface layer and a binder depleted core. The second procedure was difficult to control. It produced either pieces which were not completely dense, or if dense pieces were made, some of the binder was squeezed out. The third procedure, which could be easily controlled, resulted in high density pieces and was, therefore, used to investigate the influences of various factors on densification and transverse rupture strength. Optimum sintering conditions were found to be 1 to 2 hours at 1350°C in a vacuum of about 10^{-5} mm Hg.

The following factors had beneficial influence on densification and transverse rupture strength:

1. leaching of the ball milled TiC with hydrochloric acid
2. the use of high purity nickel as binder
3. ball milling to size and mixing with binder in one operation

4. the presence of tungsten carbide
5. an average particle size of 2 microns.

The following factors did not influence densification and transverse rupture strength:

1. the ball milling medium
2. the presence of 3% TaC
3. the presence of up to 1% oxygen
4. the presence of up to 1% iron
5. up to 2% free carbon in Metallwerk Plansee, Metro-Cutanit and Titanium Alloy TiC.

In Kennametal TiC, 1/2% free carbon lowered transverse rupture strength by almost 15% and 2% free carbon prevented densification. The presence of 3% Cr_3C_2 prevented densification during vacuum sintering.

While not all the above factors were investigated for their effects on each one of the five titanium carbide powders studied, it is believed that generally they affect all titanium carbides in a similar way. The maximum transverse rupture strengths obtained, however, were a function of the origin and, therefore, of the production procedure of the TiC powders, varying from 210,000 psi for Metallwerk to 116,000 psi for Norton powder.

SECTION V

MICROSTRUCTURE OF TITANIUM CARBIDE

A. Introduction

In spite of the fact that titanium carbides produced by different manufacturers were almost identical chemically (see Section I, Table 2), the physical properties of test bars varied considerably. It was found that the effect of production variables such as ball milling, pressing and sintering, as well as the influence of free carbon on maximum transverse rupture strength, varied with the production procedure of the original titanium carbide powders (see Tables 18, 22, 28, 29 and 32). A metallographic examination of unbonded and bonded titanium carbide bars was carried out in order to find possible reasons for these behavior differences.

For microscopic examination specimens were mounted in bakelite, ground with a 320 grit resin-bonded diamond wheel and polished on silk cloth, impregnated with Hyprez diamond paste. A detailed description of this procedure is given in a paper by R. Silverman and P. Doshna Luscz[8].

B. Microstructures of Unbonded Titanium Carbide

Experiments

Kennametal, Metallwerk, Metro-Cutanit and Norton powders were ball milled in a steel mill without the addition of a binder to average particle sizes varying from 2.1 to 2.5 microns (as measured on a Fisher Sub-Sieve Sizer) and hot pressed at about 2300°C. The densities obtained were between 90 and 95% of theoretical density. Table 33 gives the amounts of oxygen and iron after the ball milling operation. Fig. 25 shows photomicrographs of the hot pressed bars.

TABLE 33

OXYGEN AND IRON ANALYSES AFTER BALL MILLING IN STEEL MILL FOR 20 HOURS

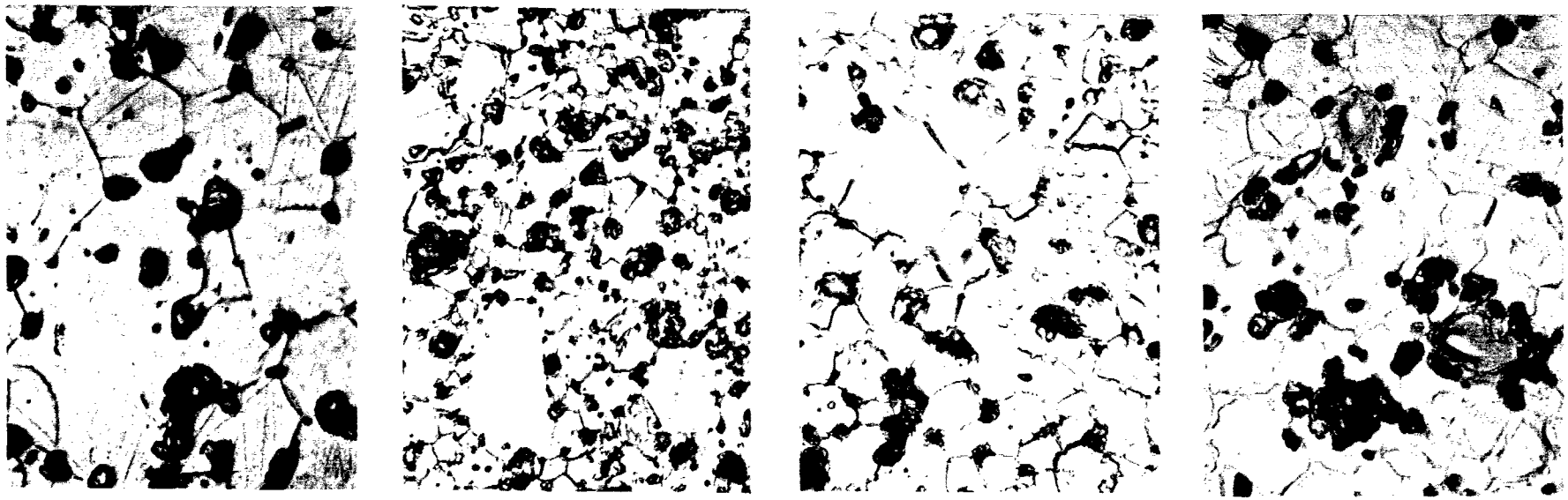
Producer	Kennametal	Metallwerk	Metro-Cutanit	Norton
Powder No.	100B	134	137	218
O_2	0.22	0.16	0.20	2.39
Fe	0.93	0.84	0.70	2.76

Results

It is assumed that ball milling of various TiC powders to approximately the same average particle size with identical ball milling procedures will result in a nearly identical particle size distribution. If this assumption is correct, Kennametal TiC when hot pressed shows grain growth to a much higher degree than any of the other three powders (Fig. 25a). Almost all the small particles have disappeared. Large grains are in evidence and these apparently have grown at the expense of the smaller ones.

Similar tendencies can be observed on the Norton TiC (Fig. 25d). Its photomicrograph looks, however, like a two-phase material, showing a fairly continuous carbide phase with what appears to be some binder (liquid phase) inclusions. There is hardly any doubt that a liquid phase consisting possibly of iron or iron carbide was present during hot pressing. Other inclusions which are clearly visible in the photomicrograph are impurities. Grain growth has taken place to a larger extent than in Metallwerk and Metro-Cutanit powders, but not as much as in Kennametal powder. There are more small grains than in the structure resulting from the Kennametal powder but less than in the case of Metallwerk and Metro-Cutanit powders.

Metallwerk and Metro-Cutanit materials present pictures very similar to each other (Figs. 25 b and c). They show nearly the same maximum grain size and a similar grain size distribution. It appears that coalescense of grains has proceeded to a greater extent in the case of Metro-Cutanit than in the case of Metallwerk material. It is probable that some grain growth



	a	b	c	d
	Kennametal	Metallwerk Plansee	Metro-Cutanit	Norton
Particle Size (microns)	2.5	2.1	2.3	2.3

Figure 25. Powders Ball Milled in Steel Mill and Hot Pressed without Binder

Etched with 1:1 20% $K_3Fe(CN)_6$ + 20% KOH

Magnification 1000 X

has taken place in both materials, with the largest grains having a diameter of about 25 microns.

Conclusions

The growth rate of particles during hot pressing or sintering is a characteristic of the particular powder. Kennametal powder shows a tendency toward grain growth to a high degree and it is believed that the reason for this can be found in its production procedure. This powder is produced by a menstruum type process, resulting in fairly large and well-formed single crystals of TiC. These crystals are broken up by grinding and ball milling, and the small fragments obtained have a much higher surface energy than the same size particles of Metallwerk or Metro-Cutanit powders. The latter two powders can be produced in a small particle size, if so desired, by taking TiO_2 of small particle size as a starting material and reacting it in the solid state with carbon. The influence of the particle size of the starting material on the particle size of the product is well known and described in the literature on tungsten carbide. Norton TiC is produced by arc-melting and it can be assumed that in this process large crystals will form on solidification of the molten mass. The amount of impurities, especially iron, present in this low priced "technical product" is large enough to form, during hot pressing, a liquid binder which is clearly visible in the photomicrograph of Fig. 25d. Other impurities form "inclusions".

C. Microstructures of Bonded Titanium Carbide Ball Milled in Steel Mill.

Experiments

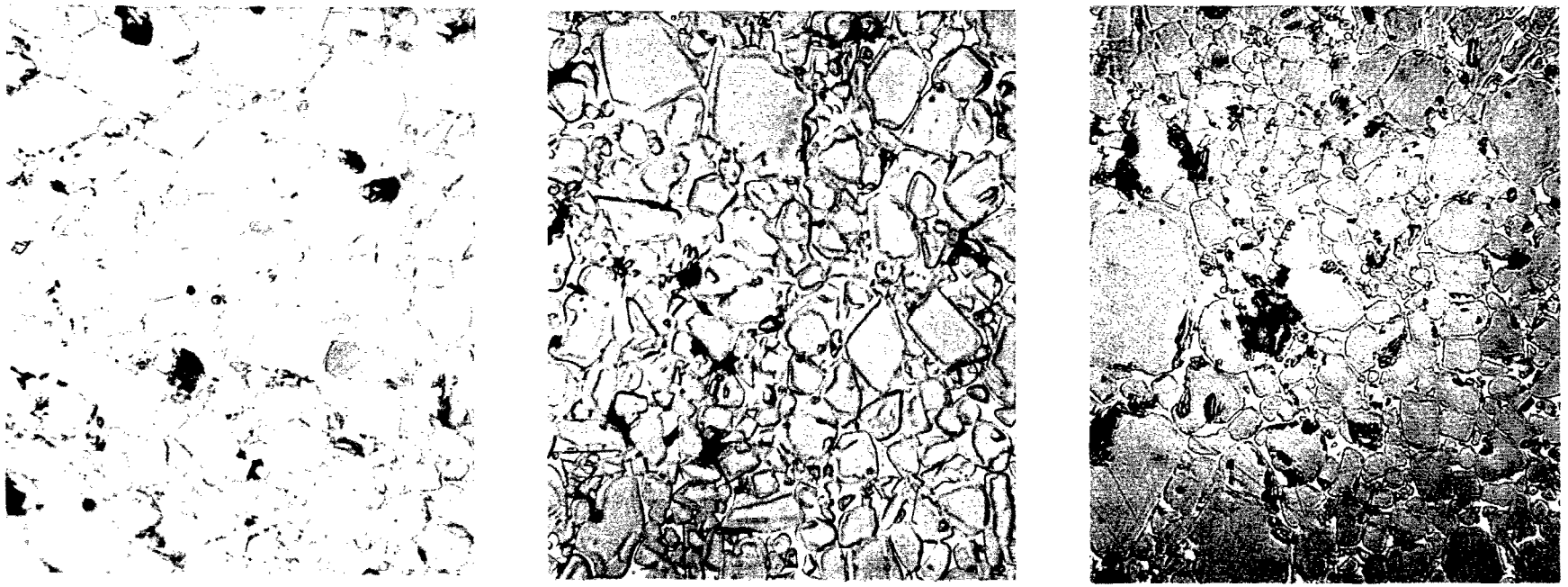
Kennametal, Metallwerk and Metro-Cutanit materials were ball milled to about 2 microns particle size in a steel mill and then ball mill mixed with 20% nickel for 20 hours, hot pressed, and vacuum sintered. Fig. 26 shows photomicrographs of this group.

Results

Kennametal powder shows a considerable tendency toward grain growth (Fig. 26a). The number of smaller particles has decreased, but to a somewhat lesser degree than in the unbonded specimen (see Fig. 25a). The tendency of the carbide grains to coalesce is clearly evident. The density of 98% and the low transverse rupture strength of 111,000 psi is probably caused by the large grain size. Almost all grains show a slight amount of coring.

Metallwerk Plansee powder, although showing grain growth, still has a large amount of small particles and a better distribution of binder and carbide due to the relative absence of the coalescing tendency (Fig. 26b). There is a high tendency of coring visible in all grains. The high transverse rupture strength of 179,000 psi and a density of nearly 100% is probably due to the large amount of small grains completely surrounded by the binder phase.

Metro-Cutanit bars show some very large grains but also a large amount of small particles (Fig. 26c). The tendency of some of the grains to



	a	b	c
	Kennametal	Metallwerk Plansee	Metro-Cutanit
Particle Size (microns)	2.1	2.1	2.3

Figure 26. Powders Ball Milled in Steel Mill, Ball Mill Mixed with 20% Nickel, Hot Pressed and Vacuum Sintered

Density (g/cc)	5.28	5.38	5.21
TRS (psi)	111,000	179,000	142,000

Sodium Picrate Electrolytic Etch. Magnification 1000 X

coalesce is clearly visible. It is not understood why this material, having a good density and a grain size distribution similar to Metallwerk material, should have a transverse rupture strength of only 142,000 psi.

The tendency to form round grains is most pronounced with Kennametal material and somewhat less with Metro-Cutanit. Most grains of the Metallwerk powder preserve their angular shape. Norton powder was not included in this group.

Conclusions

The most obvious differences between Kennametal and Metallwerk materials visible in Figs. 26a and b are the tendency of the adjacent grains to sinter together in the Kennametal product and the strong coring of practically each grain of the Metallwerk product. An explanation for the "sintering mechanism" of the Kennametal product has been proposed in the previous chapter (p. 77). Coring is most pronounced with Metallwerk powders. It occurs, however, also with others, especially with Metro-Cutanit and to a much lesser degree with Kennametal. Transverse rupture strengths of cored materials are higher than of those not showing this effect. X-ray diffraction patterns and electron microscope studies of cored materials did not reveal anything which could be used as a possible explanation for this phenomenon. The following thoughts are offered only as a probability and should be considered as such. During ball milling all powders pick up oxygen, at least part of which is present as a film of TiO_2 around the individual particles (see Section I, Table 9). During hot pressing and vacuum sintering the powders may lose some of this oxygen or may retain it all, as numerous analyses show. The oxygen still present may be in the form of an oxide film or may be in solid solution as TiO in TiC. It is believed that at least part of the oxygen is present as a film in cases where coring occurs. From infiltration experiments it is known that such an oxide film has excellent wetting properties (see Section III). TiC dissolved in the nickel binder may be precipitated on this film and protect it from being reduced by free carbon present in the binder phase. The presence of the oxide as a layer now acts as a boundary between the original grain and the precipitated TiC. These three regions give the appearance of what is called a "cored" grain. Growth of the original grain can now occur only by diffusion of TiC through the oxide layer.

D. Microstructures of Bonded Titanium Carbide Ball Milled to Size and Mixed with Binder in a Tungsten Carbide Mill (In Two Operations)

Experiments

Kennametal, Metallwerk, Metro-Cutanit and Norton powders were ball milled in a tungsten carbide mill to about 2 microns particle size, mixed with 20% nickel by further ball milling for 20 hours, and then hot pressed and vacuum sintered. Table 34 gives the oxygen and tungsten carbide analyses of these powders after the second ball milling and Figs. 27 and 28 show their microstructures.

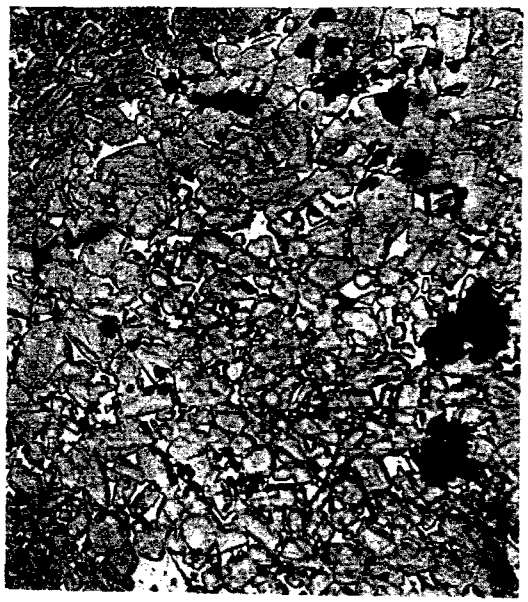
a

Kennametal

Particle Size (microns) 1.9

Density (g/cc) 5.48

TRS (psi) 153,000



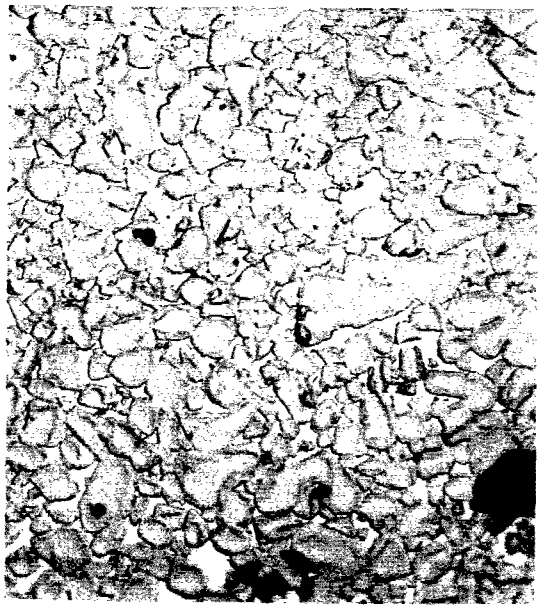
b

Metallwerk Plansee

1.95

5.48

176,000



c

Metro-Cutanit

2.3

5.40

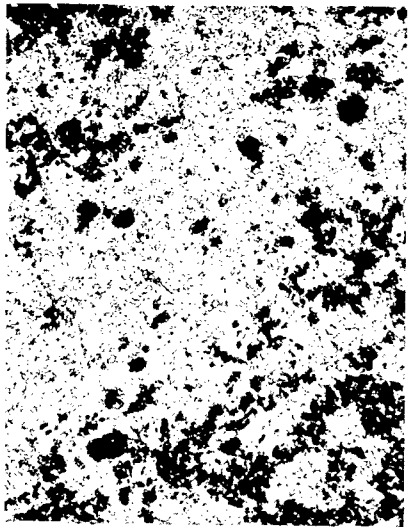
152,000

Figure 27. Powders Ball Milled in WC Mill, Ball Mill Mixed with 20% Nickel, Hot Pressed and Vacuum Sintered

Sodium Picrate Electrolytic Etch. Magnification 1000 X

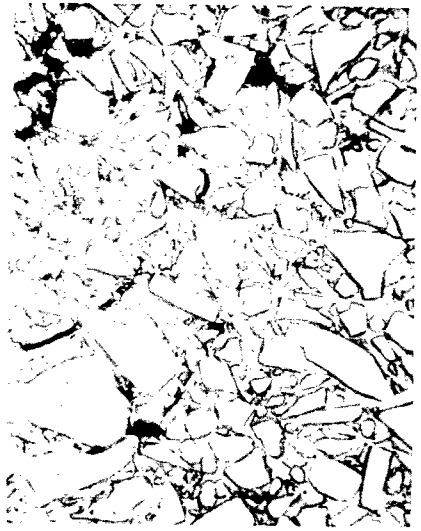
1000 X

Fig. 28a



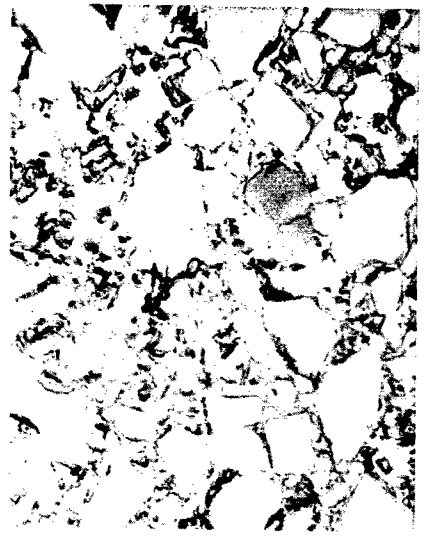
250 X

Fig. 28b



1000 X

Fig. 29



1000 X

Fig. 30

	Norton Powder	Kennametal Powder	
Particle Size (microns)	1.9	2.9	2.05
	Ball Milled in WC Mill, Ball Mill Mixed with 20% Ni, Hot Pressed, and Vacuum Sintered	Ball Milled in Steel Mill in H_2O, Ball Mill Mixed with 20% Nickel and Hot Pressed	Ball Milled in Steel Mill, Ball Mill Mixed with 3% WC and 20% Nickel, Hot Pressed and Vacuum Sintered
Density (g/cc)	4.80	5.08	5.42
TRS (psi)	69,000	50,000	148,000

Sodium Picrate Electrolytic Etch

As a comparison, Kennametal powder was also ball milled in a steel mill with steel balls to about 2 microns and then mixed with 3% tungsten carbide and 20% nickel by further ball milling for 20 hours in the steel mill. Fig. 30 shows the microstructure of a vacuum sintered bar from this material.

TABLE 34

OXYGEN AND TUNGSTEN CARBIDE ANALYSES

AFTER BALL MILLING IN TUNGSTEN CARBIDE MILL

Producer	Kennametal		Metallwerk		Metro-Cutanit		Norton
Powder No.	195[1]	208[2]	199[1]	193[2]	209[1]	211[2]	197[1]
O_2	0.90	0.43	0.45	0.32	0.42	0.22	2.24
WC	4.0	3.2	5.0	3.5	2.0	1.4	3.2

1) Ball milled for 72 hours, then 20% Ni added and ball mill mixed for 20 hours.
2) TiC + 20% Ni ball milled to size and mixed simultaneously for 72 hours.

Results

In all four materials grain growth is much less than in the previous group (Fig. 26). Kennametal and Metro-Cutanit look similar (Figs. 27a and c). Coring of grains is a little more pronounced in Metro-Cutanit than in Kennametal and both have a continuous carbide skeleton. There is a precipitate of fine, dark particles in Kennametal which is not present in Metro-Cutanit. X-ray diffraction analysis of Kennametal revealed the presence of a small amount of unidentified impurities and a trace of free WC. With structures of Kennametal and Metro-Cutanit more nearly alike, transverse rupture strengths are virtually identical.

Metallwerk Plansee powder particles show a high tendency to sinter to each other (Fig. 27b). Coring is very pronounced. Its transverse rupture strength is higher than for Kennametal and Metro-Cutanit and the same as for Metallwerk Plansee of the previous group (Fig. 26b), although the microstructures are quite different.

There is a tendency to form spherical particles which is pronounced with Metro-Cutanit material, less with Metallwerk Plansee, and indicated in the Kennametal product only by a rounding of edges.

The Norton TiC looks entirely different from the other three materials (Fig. 28a). There is no rounding of particles and hardly any coring. It looks heterogeneous, probably due to its high impurity content. The photomicrograph shows a fairly dense structure. This is deceiving, however, since the pore distribution is not uniform, as a photomicrograph of

the same specimen at 250X shows (Fig. 28b). This material looks somewhat unsintered and to a certain degree similar to a Kennametal powder which was ball milled in water and then hot pressed but not sintered, a photomicrograph of which is shown in Fig. 29.

The Kennametal material ball milled in a steel mill with the addition of 3% WC shows pronounced grain growth, angular particles, and considerable precipitation of fine particles in the binder phase (Fig. 30). X-ray diffraction anaylsis also revealed here the presence of a small amount of free WC. Although the microstructures of the two bars produced from Kennametal powder are different (Figs. 27a and 30), the densities obtained in vacuum sintering as well as the transverse rupture strengths are practically identical.

Conclusions

WC picked up from the ball mill seems to prevent excessive grain growth although there is ample opportunity for such growth. Fig. 27c, for instance, shows a fairly uniform grain size and tendency toward spheroidization of grains which is an indication of solution and precipitation of TiC from the binder phase. This picture also shows the presence of lakes of binder which would provide the necessary space to grow into.

Simple mixing (addition) of WC and TiC does not have this growth inhibiting influence, as Fig. 30 reveals.

The strictly angular grains of Figs. 28a and 29 might be due to the high oxygen content of the materials which amounts to 1.46% for the material pictured in Fig. 28a and to 1.2% for Fig. 29. The TiC-WC mixture of Fig. 30 has a fairly high oxygen content of 0.58%. It has been reported for WC that powders of high oxygen content sinter with greater difficulty and that the grain size of the sintered product is less than with powder of low oxygen content[9]. The same might be true for titanium carbide.

E. Microstructures of Bonded Titanium Carbide Ball Milled to Size and Mixed with Binder Simultaneously in Tungsten Carbide Mill

Experiments

Kennametal, Metallwerk Plansee and Metro-Cutanit powders were ball milled to size and mixed with 20% nickel simultaneously in a tungsten carbide mill for 72 hours, and hot pressed and vacuum sintered under identical conditions. Fig. 31 shows the microstructures and Table 34 gives oxygen and tungsten carbide analyses after ball milling.

Results

A moderate grain growth occurred in all three powders. Coring is evident with all of them but much more pronounced with Metallwerk and Metro-Cutanit materials (Figs. 31b and c) than with Kennametal (Fig. 31a). Practi-

cally all grains of these first two powders show coring. Despite the grain growth, there are many small grains present. This is probably the reason for the good densification obtained and for the high transverse rupture strengths. Comparing this group with Fig. 27, Kennametal and Metro-Cutanit in both groups present very similar pictures. Metallwerk Plansee (Fig. 27b) shows a continuous carbide mass with interspersed larger or smaller lakes of binder, while Fig. 31b shows distinctly separated grains, highly cored, with uniform binder distribution. This microstructure showed the highest transverse rupture strength (198,000 psi) obtained in this investigation, and it is interesting to note that practically identical structures obtained with the same Metallwerk powder after ball milling in a steel mill (Fig. 26b) have the second highest transverse rupture strengths (179,000 psi).

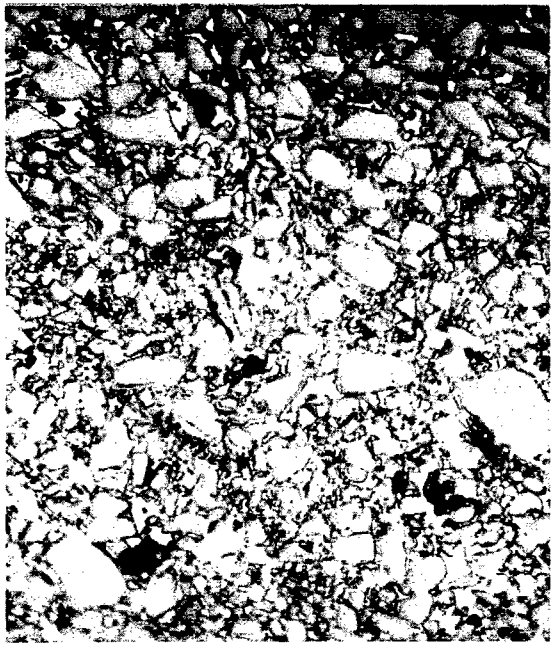
Conclusions

Comparing the photomicrographs and the transverse rupture strengths of the materials discussed in this and the foregoing two chapters, it must be concluded that the following microstructure is the most desirable: highly cored angular shaped particles surrounded completely by the binder phase which has almost the character of a film. No binder lakes should be present. A certain amount of grain growth is tolerable as long as there are enough small and medium sized grains present to insure a dense packing.

It is quite conceivable that changes in sintering conditions could produce this "ideal structure" for Metro-Cutanit and Kennametal materials pictured in Figs. 31c and a. The great differences between Kennametal and Metro-Cutanit materials pictured in Figs. 26a and c, and the Metallwerk product shown in Fig. 26b, and the similarity of this latter product with the one shown in Fig. 31b might have its cause in the small amounts of tungsten (and probably molybdenum) present in the as-received Metallwerk powder. This small amount of tungsten might also be the reason for the restriction of grain growth of the unbonded Metallwerk TiC (Fig. 25b).

It appears that ball mill mixing and sizing in one operation leads to thoroughly nickel coated carbide particles in contrast to a poorer nickel to carbide distribution for the separate operations. The thin film surrounding each particle more uniformly and not as randomly, insures a better preparation of this powder for sintering. The fact of superior transverse rupture strengths of the thus prepared materials, especially Metallwerk powder, might be attributed to a better "packing factor". Obviously, a more favorable fine to coarse grain ratio results in better packing and takes better advantage of more nickel coated surfaces contributing towards a more complete bonding during sintering.

In this connection reference is made to an article by Norton[10] dealing with a theory of "stronger bonding through thinner films". It is possible that those thoughts could also be applied to the discussion above.



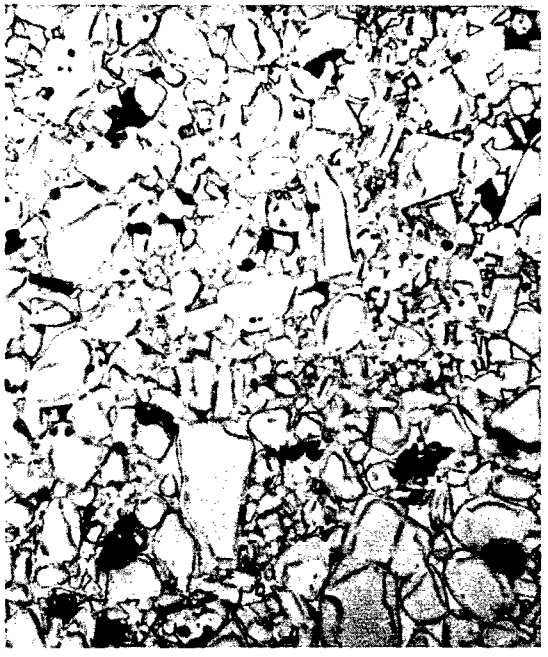
a

Kennametal

Particle size (microns) 1.7

Density (g/cc) 5.44

TRS (psi) 161,000



b

Metallwerk Plansee

2.2

5.41

198,000

c

Metro-Cutanit

2.4

5.39

166,000

Figure 31. Powders Ball Milled to Size and Mixed Simultaneously with 20% Ni in WC Mill, Hot Pressed and Vacuum Sintered

Sodium Picrate Electrolytic Etch. Magnification 1000 X

F. Influence of Ball Milling Medium on Microstructure

Experiments

Kennametal powder was ball milled to size and mixed simultaneously with 20% nickel for 72 hours in a tungsten carbide mill using carbon tetrachloride, hexane, ethyl alcohol, and acetone, respectively, as ball milling media. The powders were vacuum dried, hot pressed and vacuum sintered under identical conditions. The amounts of oxygen and tungsten carbide picked up during ball milling are given in Table 35. Figs. 32a to d are photomicrographs of the vacuum sintered bars.

TABLE 35

OXYGEN AND TUNGSTEN CARBIDE ANALYSES AFTER BALL MILLING IN VARIOUS LIQUIDS FOR 72 HOURS

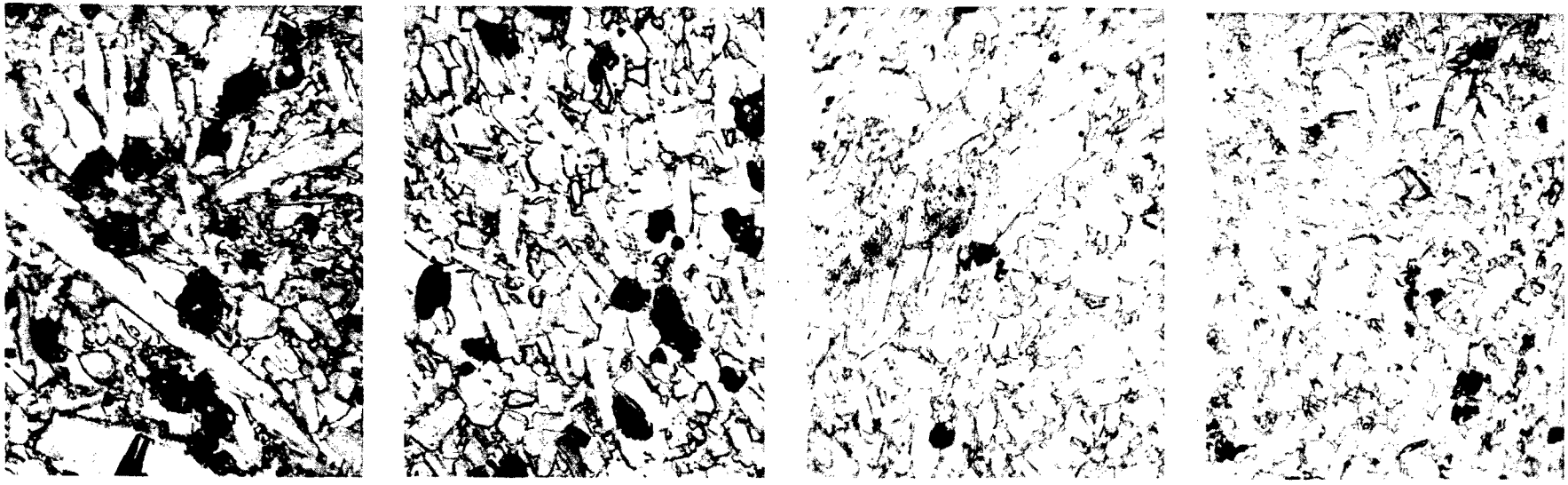
(Kennametal Powder + 20% Ni)

Powder No.	Carbon Tetrachloride 214	Hexane 215	Ethyl Alcohol 216	Acetone 217
O_2*	0.53	0.47	0.31	0.50
WC	3.8	5.1	3.9	4.8

* The oxygen pickup during ball milling in a liquid was a function of the air space left in the ball mill. In these experiments the ball mill was filled almost to the top with liquid. As a consequence, the O_2 pickup was about the same as when ball milling was done in air. If the ball mill was only filled partly with the liquid, the O_2 pickup was considerably increased (see Section I, Chapter B).

Results

The photomicrographs show the formation of elongated grains. This uni-directional grain growth is especially pronounced with carbon tetrachloride and acetone as ball milling media. Since in the presence of a large number of elongated grains dense packing cannot be obtained, densities and transverse rupture strengths of the materials ball milled in these two media are very low. With powders ball milled in hexane and ethyl alcohol, only some grains show uni-directional growth. Coring is found only to a minor degree, as is usually the case for Kennametal material.



a b c d

Figure 32. Kennametal + 20% Nickel Ball Milled in WC Mill in

	Carbon Tetrachloride	Acetone	Ethyl Alcohol	Hexane
Particle Size (microns)	2.2	2.2	2.3	1.7
		Hot Pressed and Vacuum Sintered		
Density (g/cc)	5.07	5.36	5.71	5.55
TRS (psi)	90,000	119,000	144,000	144,000

Sodium Picrate Electrolytic Etch. Magnification 1000 X

Conclusions

The presence of a large number of elongated grains makes dense packing impossible. The transverse rupture strengths obtained with powders ball milled in carbon tetrachloride and acetone are therefore low.

As it is inconceivable that these elongated grains could have formed during ball milling, they must have formed during hot pressing and vacuum sintering. Nevertheless, it is believed that the reason for their formation lies in the ball milling medium. (Compare with Fig. 31a, which shows the microstructure of the same material ball milled in air). Certain ball milling media give the particles a surface conditioning which enhances grain growth. Where grain growth is not so pronounced, the picture shows a non-uniform binder distribution (especially visible in Figs. 32c and d) which is not desirable.

G. Influence of Pressing Procedure on Microstructure

Experiments

Kennametal powder with the addition of 20% nickel was ball milled in a tungsten carbide mill with carbon tetrachloride as ball milling medium for 144 hours in order to get very small particles (1 micron). The powder was compacted by three different pressing procedures in order to compare their effectiveness. It was:

a. cold pressed in the wet condition (wet pressed),
b. dried and cold pressed after 3% camphor had been added, and
c. dried and hot pressed.

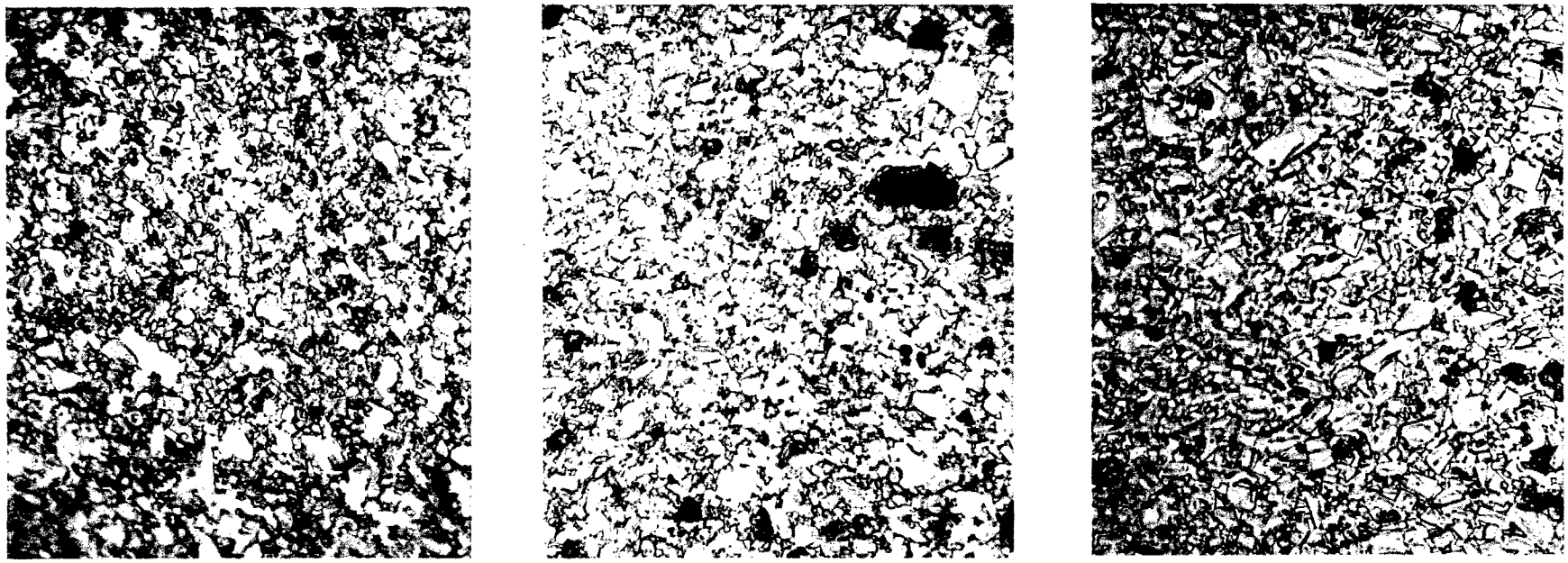
Results

The microstructures obtained with these three procedures are very similar (Fig. 33). The tendency to grain growth is the least in the wet pressed bars, somewhat more in the cold pressed bars and quite pronounced in the hot pressed bars. Elongated grains can be found, especially in the hot pressed pieces, but to a far lesser degree than in the previous group, so that dense packing is still possible. Practically every grain of the hot pressed bar shows coring, but this can also be found with wet and with dry cold pressed pieces, though to a much lesser degree.

Densities obtained with all three procedures are identical, but transverse rupture strengths of wet and hot pressed bars are superior to cold pressed bars.

Conclusions

Some workers in the field of cermets recommend carbon tetrachloride as a ball milling medium, and the results of these experiments show that good densities and high transverse rupture strengths are obtainable using it. However, there seems to be one condition. Ball milling has to be done for a long time in order to get a small enough particle size. By vacuum sintering



a b c

Figure 33. Kennametal + 20% Nickel Ball Milled in WC Mill in Carbon Tetrachloride
Particle Size 1.0 micron

	Wet Pressed	Cold Pressed	Hot Pressed
		All Pieces Vacuum Sintered	
Density (g/cc)	5.43	5.48	5.46
TRS (psi)	170,000	139,000	161,000

Sodium Picrate Electrolytic Etch. Magnification 1000 X

of hot pressed bars, grains grow and form elongated shapes to a higher degree than by sintering of wet or cold pressed bars, but due to the original small particle size, they are still small enough to allow dense packing. Coring is still prevalent with grains of the hot pressed and vacuum sintered specimen. Fig. 33c resembles closely Figs. 26b and 31b, which are considered to have the best obtainable microstructures. The presence of coring was linked above to an oxide film. The powder used for these experiments had an oxygen content of 1.7% after ball milling. Hot pressing reduced this amount to 0.53% and the following vacuum sintering to 0.35%. Wet pressed or cold pressed and vacuum sintered bars showed an oxygen content of 0.2 and 0.17%, respectively. The high vacuum seems to destroy the oxide film before sintering occurs. The transverse rupture strength of cold pressed and vacuum sintered bars is inferior to those wet or hot pressed. This might have its cause in the non-uniform distribution of fairly large pores.

H. Influence of Sintering Procedure on Microstructure

Experiments

Metallwerk Plansee powder was ball milled to size and mixed with 20% nickel simultaneously in a tungsten carbide mill for 192 hours. The average particle size obtained was 1.8 microns. The powder was mixed with 2% camphor and cold pressed at 10 tsi.

The following sintering experiments were made with these bars:

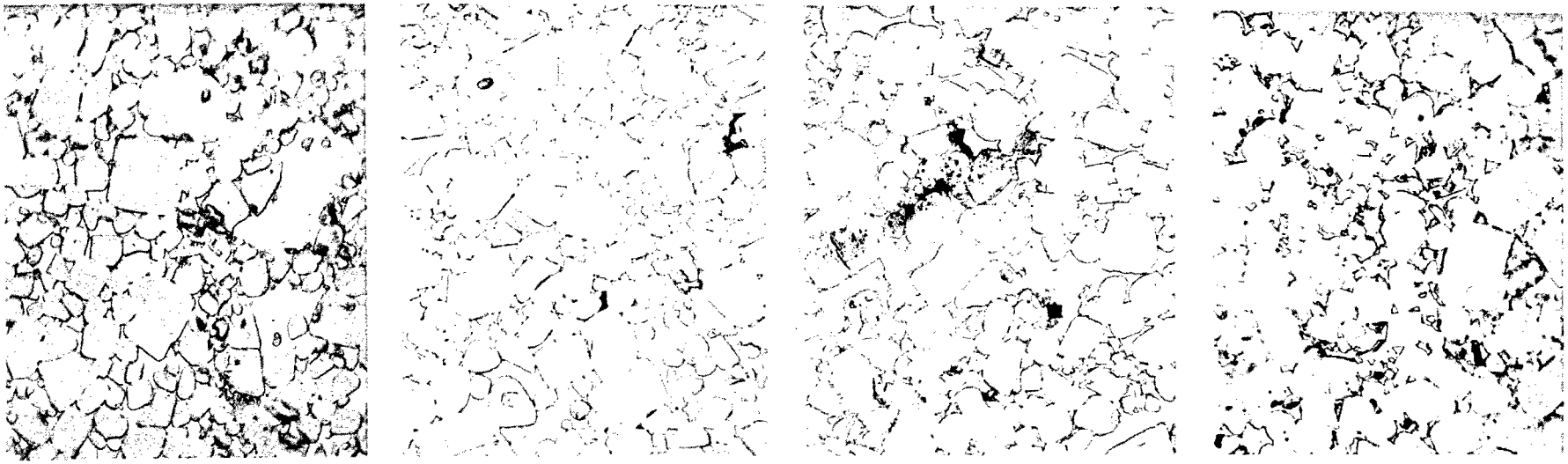
1. The first set was sintered for 2 hours at 1350°C in a vacuum of 5×10^{-5} mm Hg, resintered for one hour at 1400°C in a vacuum between 50 and 100 microns, and sintered a third time for one hour at 1420°C in a vacuum between 50 and 100 microns.
2. The second set was sintered for 2 hours at 1350°C in a vacuum of 5×10^{-5} mm Hg and resintered for 1/2 hour at 1500°C in a vacuum between 50 and 100 microns.
3. The third set was sintered for 30 minutes at 1500°C in a vacuum between 50 and 100 microns.
4. The fourth set was sintered for 5 minutes at 1520°C in a vacuum between 50 and 100 microns.

For an additional experiment, Metallwerk powder was ball milled in a steel mill with tungsten carbide balls to a particle size of 1.6 microns and mixed with 20% nickel for 20 hours under the same ball milling conditions. This powder was cold pressed as above and the bars vacuum sintered for 30 minutes at 1530°C.

A low vacuum of 50 to 100 microns was used with temperatures above 1350°C in order to avoid loss of binder.

Results

The densities obtained in the first experiment were 5.25 g/cc, 5.30 g/cc, and 5.36 g/cc, respectively, after the three sinterings (Fig. 34a).

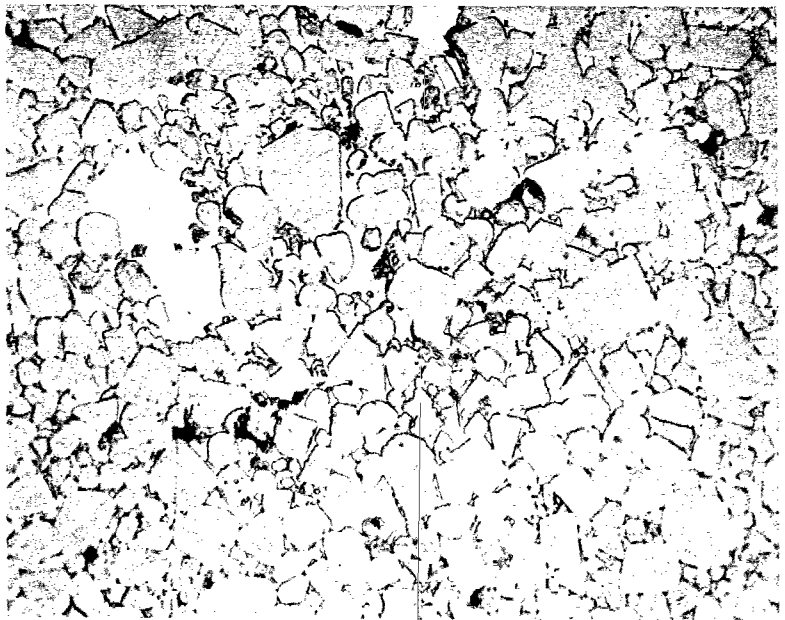


a b c d

Figure 34. Metallwerk Plansee + 20% Nickel Ball Milled in WC Mill (1.8 microns), Cold Pressed and Vacuum Sintered

	a	b	c	d
	2 hrs. at 1350°C 1 hr. at 1400°C 1 hr. at 1420°C	2 hrs. at 1350°C 1/2 hr. at 1500°C	1/2 hr. at 1500°C	5 min. at 1525°C
Density (g/cc)	5.36	5.48	5.46	5.44
TRS (psi)	140,000	138,000	138,000	127,000

Sodium Picrate Electrolytic Etch. Magnification 1000 X



Sodium Picrate Electrolytic Etch

1000 X

Fig. 35

Metallwerk Plansee Ball Milled in Steel Mill with WC Balls, Ball Mill Mixed with 20% Nickel, Cold Pressed and Vacuum Sintered (1/2 hour at 1530° C)

Density	5.47 g/cc
TRS	128,000 psi

After the two sinterings of the second experiment, densities were 5.26 g/cc and 5.48 g/cc, respectively (Fig. 34b). Experiments 3 and 4 were made after it was found that a higher temperature was necessary to obtain good densification. The densities obtained after these experiments were 5.46 g/cc and 5.44 g/cc, respectively (Figs. 34c and d). The additional experiment produced bars with a density of 5.47 g/cc (Fig. 35).

The microstructures obtained were completely identical. Astonishingly, a bar sintered for 4 hours at temperatures up to 1420°C did not show larger grain growth than a bar held at 1520°C for 5 minutes. There is a continuous carbide skeleton formation which is not further advanced after 4 hours than after 5 minutes. There is no evidence of coring, although Metallwerk Plansee powder when hot pressed shows this phenomenon to an especially high degree. With microstructures and final densities practically identical, strengths were also the same, as expected (127,000 psi to 140,000 psi). The presence of 1% iron did not change the microstructure as Fig. 35 shows.

Conclusions

The fact that the five pictures presented in this chapter are completely identical in microstructure, makes it appear as if grain growth took place only in the initial stage of the sintering process. The reason for this is unknown. The presence of 4% WC after ball milling might here again have prevented excessive grain growth, although binder lakes are available to supply the necessary space for growing grains. Coring, which is especially characteristic of Metallwerk Plansee powders, did not occur, probably due to the lack of an oxide film. The powders as ball milled had an oxygen content of about 0.6%, and after sintering of only 0.1%. The high vacuum seems to have destroyed this film before sintering has started, as mentioned above.

The non-uniform binder distribution, the presence of large lakes, and the absence of coring are the reasons for the inferior transverse rupture strength of this material although the obtained densities are satisfactory.

I. General Conclusions

Three mechanisms have been proposed as an explanation for grain growth[11]. They are:

1. Coalescence of adjacent grains,
2. Solution in the binder phase during heating and reprecipitation during cooling, and
3. Transfer of carbide from smaller to larger grains by diffusion through the liquid binder.

Only the first of these mechanisms can take place in the absence of a binder. In the presence of a binder, it is impossible to state in each case which one of these mechanisms was effective. Most probably all three are taking part at the same time to various degrees. It seems, however, that with Kennametal and Norton materials coalescence of adjacent grains is a

major source of grain growth unless ball milling is done in a tungsten carbide mill. The picked-up WC seems to restrict this type of grain growth (compare Figs. 26a and 27a). Addition of WC and ball milling in a steel mill has not the same effect (see Fig. 30).

It is believed that the second mechanism, solution and precipitation of TiC from the binder phase, will cause a rounding of particles which is pronounced with Kennametal and Metro-Cutanit powders, (see Figs. 26a, 27c and 31c) but also occurs to a lesser degree with Metallwerk material (Fig. 27b).

The third mechanism of grain growth, a diffusion of TiC not only through the binder phase but also through an oxide layer surrounding the original grains, is believed to be effective especially in those cases where "coring" occurs. This phenomenon is highly pronounced with Metallwerk powder (see Figs. 26b and 31b), clearly visible also in Metro-Cutanit products (see Figs. 27c and 31c) and occurs in Kennametal to a considerable degree only, if ball milling for a long time has raised the oxygen content of this material (see Fig. 33c). Vacuum sintering of cold pressed bars prevents coring even of Metallwerk material due to the elimination of oxide films in high vacuum before sintering starts (see Figs. 34 and 35). Grain growth occurs in this case mainly by sintering together adjacent particles and, as the rounding of grains indicates, by solution and reprecipitation.

The use of a liquid ball milling medium enhances grain growth and causes segregation (see Fig. 32). The latter can be counteracted by ball milling to a small particle size (see Fig. 33).

The retaining of oxygen, probably in solid solution, might have a bearing on the preservation of angular particles. The Norton product pictured in Fig. 28a has an oxygen content of 1.46% and the Kennametal bar presented in Fig. 30, 0.58%, both after vacuum sintering.

SUMMARIZING REMARKS

It can be stated that the results obtained during the course of this research are such that tentative specifications can be set up, to guide cermet manufacturers concerned with titanium carbide base materials. These specifications are along the following lines, in order to obtain materials not only satisfactory from a manufacturing and structural point of view, but also readily reproducible.

1. It has been recognized that a good TiC powder must fulfill the following criteria:

   a. Its oxygen content must be distributed in a way similar to that observed for the Metallwerk Plansee powder. The assumption is

made that the "coring" effect consists of a TiC core surrounded by a TiO_2 film or a TiC-TiO solid solution area onto which some TiC is reprecipitated. In other words, the oxygen content as such may be a criterion; and the core structure, reflecting the state in which the oxygen is contained in these materials, is of importance to obtain proper wetting with a binder phase.

b. An optimum packing factor, i.e., a certain ratio of large to small grains must be maintained. Again an attempt should be made to reproduce the particle distribution shown in photomicrographs of this report for materials with high transverse rupture strength.

c. The inclusion of tungsten carbide, as picked up during ball milling, is of importance to prevent excessive grain growth during processing and thereby retain the original particle size distribution of the powder.

d. It appears of greatest importance to obtain complete coating of the binder phase around each particle. This can be obtained only by simultaneous ball milling to size and mixing. The prevention of "binder lakes" can thus be achieved with each individual particle being thoroughly prepared for the sintering process through uniformly distributed ("smeared on") binder metal.

2. Now that the most important criteria for a good TiC base cermet powder have been specified, the following future work suggests itself, on the basis of (1.) above:

   a. Establish methods of testing powders for particle size distribution so that the packing factor of powders which yielded bars with desirable properties can be reproduced for other powders.

   b. Determine a way to incorporate oxygen (in form of TiO or TiC_2 or otherwise) into other powders so as to reproduce the coring effect observed in Metallwerk material.

   c. Learn how to prevent grain growth by balancing out the amount of tungsten carbide to be picked up against the inherent grain growth characteristics of the respective powders.

If the above results are correctly interpreted and applied to powders of all manufacturers, it should be possible to provide the Air Force with TiC base high temperature materials that should be of the highest quality regardless of the manufacturer submitting the respective parts.

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